
USING A COMPUTER WATER-QUALITY MODEL TO DERIVE NUMERIC NUTRIENT CRITERIA FOR A SEGMENT OF THE YELLOWSTONE RIVER

Quality Assurance Project Plan (QAPP)

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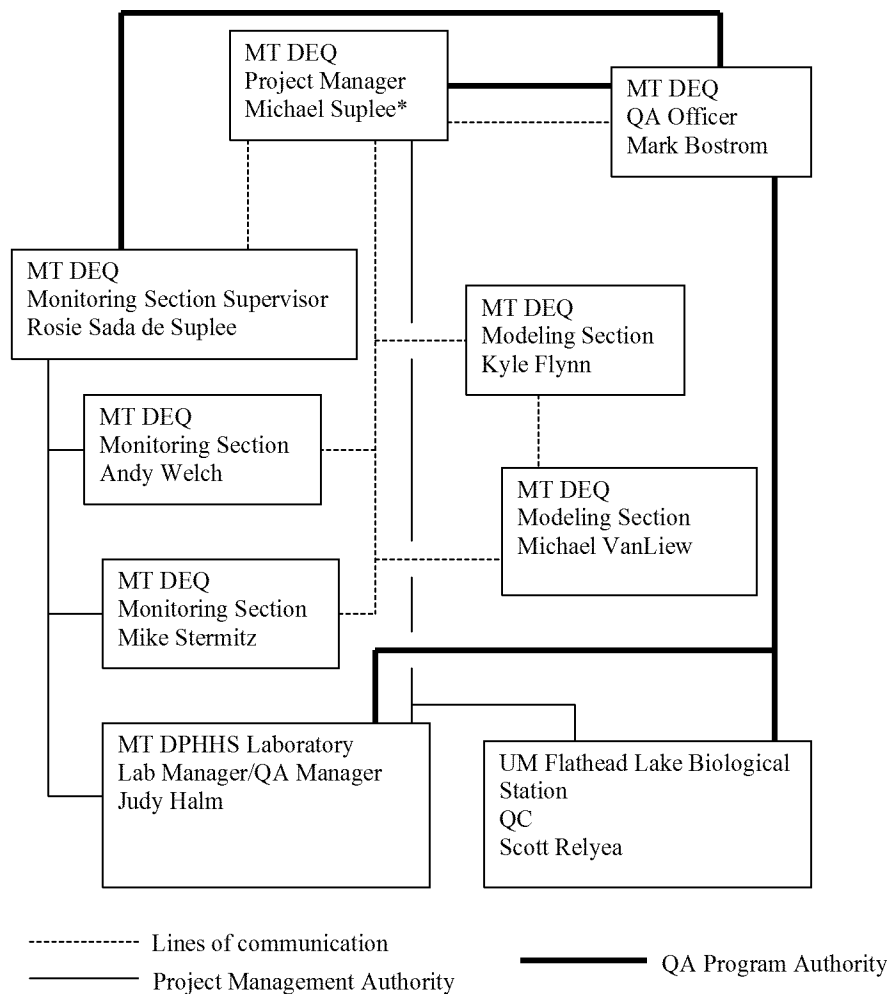
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APPENDICES

Appendix A *Data Collected on the Yellowstone River, Aug. 2006*

1.0 Project/Task Organization

This document presents the research quality assurance project plan (QAPP) for collecting and analyzing data from a segment of the lower Yellowstone River. This work is being undertaken for the purpose of developing a computer water-quality model. As such, in addition to quality assurance descriptions for field-collected data, detailed descriptions of how the computer model will be calibrated and validated are also provided herein. Field data collection and model setup/calibration-verification will be done by staff of the Montana Department of Environmental Quality (DEQ). Analysis of samples will be undertaken by the University of Montana Flathead Lake Biological Station and the Montana Department of Public Health and Human Services Environmental Laboratory. Michael Suplee, Ph.D., will provide overall project oversight for this study. The following chart shows the roles of the various entities and their relationship to one another.



* In the field, Suplee will have general management authority for sampling decisions affecting the crew.

2.0 Introduction

2.1 Background

In Montana, designated beneficial uses of state surface waters include growth and propagation of fish and associated aquatic life, drinking water, agriculture, industrial supply and recreation (ARM 17.30.621 through 629). Eutrophication, or the over enrichment of waterbodies by nutrients (usually nitrogen [N] and phosphorus [P]), can cause nuisance algal growth, alter aquatic communities and result in undesirable water-quality changes that can impair these beneficial uses (Freeman, 1986; Arruda and Fromm, 1989; Welch, 1992; Dodds et al., 1997). Since 2001, the Montana Department of Environmental Quality (DEQ) has been working to develop numeric nutrient criteria for surface waters. The intent of numeric nutrient criteria is to protect waterbodies and their associated beneficial uses from the adverse effects of eutrophication. DEQ has made good progress in nutrient criteria development for wadeable streams and small rivers of the state by integrating stressor-response and reference-based approaches (Varghese and Cleland, 2005; Suplee et al., 2007). However, criteria development for large rivers (e.g., Yellowstone, Missouri rivers) has not yet been undertaken. Herein, we propose an approach to developing numeric nutrient criteria for a large river segment using a mechanistic, computer water-quality model. This differs from the methods DEQ has used thus far for wadable streams.

2.2 Problem Definition

Montana DEQ believes that a nutrient-criteria derivation technique for large rivers (defined loosely here as river segments with a Strahler order ≥ 7 , 1:100,000 scale; Strahler, 1964) should differ from DEQ's wadeable-stream approach because (1) the ability to identify—reference|| watersheds for the state's large rivers, per the wadeable-stream methods outlined in Suplee et al. (2005), is infeasible, and (2) using reference—segment-sheds|| for large rivers (Fig. 1), per proposed EPA methods (M. Paul, personal communication) may not sufficiently address cumulative affects from upstream of the reference segment-shed. Without being able to identify reference watersheds for these large systems, setting benchmarks based *only* on reference segment-sheds becomes highly debatable. Further, in the absence of reference one is left with the task of defining a water quality impact without the benefit of knowing what un-impacted looks like.

Because of the issues outlined above, we believe that a reasonable way to proceed toward developing nutrient criteria for large rivers is to identify the valued ecological attributes of the system of concern, clearly state how these relate to beneficial uses, and then determine when those attributes have been impacted, via simulation modeling. Valued ecological attributes are defined as ecosystem characteristics that directly or indirectly contribute to human welfare (Stevenson 2006), and are closely allied with beneficial uses. Determining when valued ecological attributes/beneficial uses have been impacted can be difficult, and requires both value judgments and scientific understanding. The more clearly an impact threshold to a valued ecological attribute/beneficial-use can be defined, the more defensible will be the nutrient criteria that prevent the impact.

We propose developing numeric nutrient criteria on a large river segment through mechanistic water-quality modeling by considering two specific valued ecological attributes that can be directly linked to beneficial uses. Because there are clear impact thresholds for the following, we intend to model these on the Yellowstone River:

1. Dissolved oxygen levels, which are required by state law to be maintained ≥ 5 mg/L in order to protect aquatic life and fishery uses (early life stages; DEQ 2006a).
2. Benthic algae levels, which should be maintained below a nuisance threshold {ARM 17.30.637(1)(e)} to protect recreation uses. Based on a 2006 DEQ scientific public opinion survey addressing when the recreational use of rivers & streams becomes impacted by excess benthic algae, algae levels should be kept below 150 mg Chl *a*/m² (Larix 2006; also see study results at: <http://www.umn.edu/watershedclinic/algaeurveyipix.htm>).

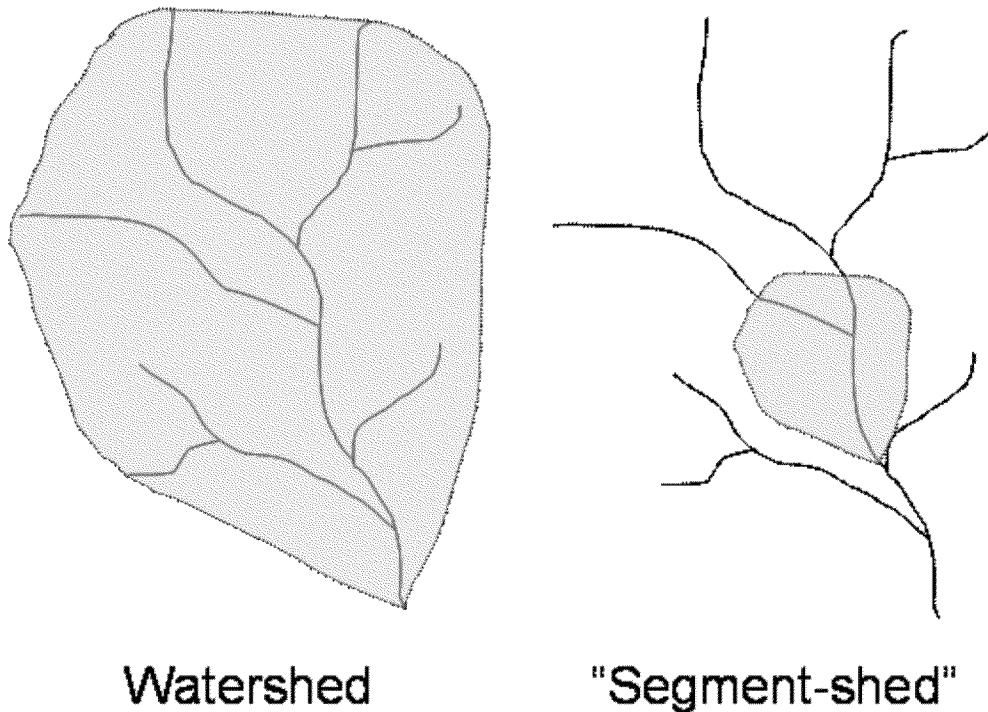


Figure 1 – Conceptual diagram illustrating the watershed versus segment-shed ideas. The segment-shed is recommended for considering the area contributing to land cover/land use information above a large river site.

The QUAL2K model was selected by DEQ for the Yellowstone project due to its frequent use in dissolved oxygen (DO) modeling and its ability to simulate benthic algae levels (Drolc and Koncan, 1996; Chaudhury et al., 1998; Chapra, 2003, USGS SMIC 2005). Although the benthic component of the model has not been well reported on in the literature, empirical relationships between river nutrient concentrations and benthic algae density have been reported (e.g., Dodds

et al. 1997). Butcher (2006) reported that the default parameters in computer models like QUAL2K need to be adjusted to come in to alignment with the empirical results of published studies (e.g., Dodds et al., 1997). DEQ acknowledges that there may be inconsistencies between mechanistic models and empirical nutrient-algae relationships, and we will carefully assess this during model development. To help cross-check the modeled criteria, two other nutrient criteria development techniques will be considered. First, a quasi-reference approach will be used whereby the modeled criteria will be compared to nutrient concentrations from an upstream reach of the Yellowstone River perceived to have minimal water quality impacts (comparison site; Suplee, 2004). Second, the model output nutrient concentrations will be compared to concentrations from river and stream empirical models (Dodds et al., 1997; Dodds et al., 2006). These efforts will help cross-check the model output results.

Based on preliminary discussions among the principle authors of this QAPP (Suplee, Flynn and Van Liew, DEQ), it was decided to undertake the modeling work on a segment of the lower Yellowstone River. The segment was selected because it has a minimal number of point sources, a fairly well established gaging network, and fairly characteristic non-point source impacts. Further, Miles City (within the study reach) is currently in the planning phase of upgrading its wastewater treatment plant. As part of this upgrade, Miles City is very interested in potential future numeric nutrient criteria that may apply to the Yellowstone River. To assure that this segment of the Yellowstone River was appropriate for the project, reconnaissance trips by DEQ staff were undertaken along the river from August 14th – 19th 2006, February 7th – 8th 2007, and June 21st-22nd, 2007. During these trips notes were taken on the accessibility of various locations along the reach, candidate locations to install monitoring equipment were identified, and field measurements of stream velocity, DO, temperature and sediment oxygen demand (SOD) were made.

3.0 Project/Task Description

3.1 Primary Question, Objectives and River Reach Description

The project outlined in this QAPP is designed to answer the following question:

In a segment of the lower Yellowstone River, what are the highest allowable concentrations of nitrogen and phosphorus which will not cause benthic algae to reach nuisance levels and/or dissolved oxygen concentrations to fall below applicable State water quality standards?

As described previously, DEQ intends to use a computer model that will answer this question. The Yellowstone River segment to be modeled will extend from the Rosebud West fishing access site (FAS) at 46.2646 N latitude, 106.6959 W longitude (just upstream of USGS gage 06295000 Yellowstone River at Forsyth, MT), to the old Bell Street Bridge at 47.1055 N latitude, 104.7198 W longitude, which is at the same location as USGS gage 06327500, Yellowstone River at Glendive, MT (Fig 3.1).

Once the model is calibrated and validated (Chapra, 2003; Wells, 2005) for this reach, DEQ will simulate a critical low-flow condition (i.e., 7Q10) during which nuisance algae growth and

depressed DO concentrations are likely to be most severe. We will then vary N and P concentrations in the model to affect changes in the DO and algae-level outputs from the model. The highest input N (dissolved organic N, NO_3 , and NH_4) and P (dissolved organic P and inorganic P) concentrations that do not cause nuisance algae growth and/or exceedences of the DO standard under these low-flow conditions can be used as the numeric nutrient criteria for this river segment during the base flow period. Total to soluble nutrient ratios — as currently manifested in the river — will be used to derive total nutrient criteria concentrations, which are the end goal of this project. If a single nutrient (e.g., N) is clearly limiting in the river, the Redfield ratio (Redfield, 1958) will be used to set the accompanying, non-limiting nutrient criterion.

In order to accurately calibrate & validate the model, DEQ intends to measure a large number of factors that directly or indirectly influence DO and benthic algae density in the river. These include forcing functions such as meteorology and hydrology, and state/rate data, which are described in subsequent sections. Our basic assumption is that direct measurement of key parameters will increase the confidence in the model predictions and reduce the uncertainty in model parameters and coefficients (Melching and Yoon, 1996; Barnwell et al., 2004). The modeled criteria can also be compared to nutrient concentrations from the upstream comparison site on the Yellowstone River perceived to have minimal water quality impacts, and to results from applicable empirically-derived models (Dodds et al. 1997; Dodds et al. 2006).

3.2 Project Design

3.2.1 Model Selection

The criteria for selecting a model were (A) relative simplicity and (B) its ability to answer our question and yield adequate accuracy (Krenkel and Novotny, 1979; Chapra, 2003). QUAL2K, MIKE11, WASP, and CE-QUAL-W2 were all considered. QUAL2K was ultimately selected by DEQ due to frequency in application for TMDL planning and dissolved oxygen modeling (Drolc and Koncan, 1996; Chaudhury et al., 1998; Rauch et al., 1998; Chapra, 2003, USGS SMIC, 2005), endorsement by the EPA (EPA, 2005) and because it offers relative simplicity as a one-dimensional steady-state model (e.g., it assumes the channel is well mixed vertically and longitudinally and meteorology, hydrology, and hydraulics remain constant during the simulated time-step). QUAL2K can also be run in a quasi-dynamic mode to simulate diurnal DO and temperature variations (Mills et al., 1986; Chapra and Pelletier, 2003). The other models that were considered are fully dynamic, but are more complex and require more data input, and one (MIKE11) is proprietary. QUAL2K is also able to simulate benthic algae growth, a key parameter of interest in this study, which its predecessor (QUAL2E) could not.

DEQ measured DO and temperature during the summer 2006 reconnaissance trip to verify that basic modeling assumptions such as complete mixing (vertically and laterally) would not be violated at any of the sites visited. The results of the field work are documented as part of this QAPP (Appendix A) and clearly show that the initial model assumptions are satisfactory. In addition, the steady state flow assumption was evaluated using the anticipated headwater flow at the Forsyth USGS gage. Over a one week period from August 15-22 (the anticipated period for modeling) flow changed 6% of the period of record. This is considered acceptable for steady-state modeling.

3.2.2 Model Development and General Design

Seven major river subreaches, which comprise the entire Yellowstone River study reach, were identified for model development. Each of the seven major subreaches will be further subdivided based on hydrology, hydraulics, known water quality changes, etc. such that approximately 30-40 total modeling subreaches are anticipated. The seven major subreaches are (Figure 3.1): (1) Rosebud West FAS to the Cartersville Canal return flow, (2) Cartersville Canal return flow to the Tongue River confluence; (3) Tongue River confluence to Kinsey Bridge FAS, (4) Kinsey Bridge FAS to the Powder River/Shirley Main Canal confluence; (5) Powder River/Shirley Main Canal confluence to the O'Fallon Creek confluence, (6) the O'Fallon Creek confluence to eleven miles upstream of Glendive, MT, and (7) eleven miles upstream of Glendive to the Bell Street Bridge in Glendive, MT. A YSI 6600EDS sonde will be deployed at each of these breakpoints and will measure the necessary parameters for water-quality model calibration (temperature, DO, pH, Chl *a*, etc.). Additionally, an upstream site will be located at the Buffalo Mirage FAS just upstream of Laurel, MT. The comparison site is on an upstream segment of the Yellowstone River currently considered to fully support all its uses (2006 Integrated Report), and is near or within the ecotone where the river changes from a cold-water to a warm-water fishery.

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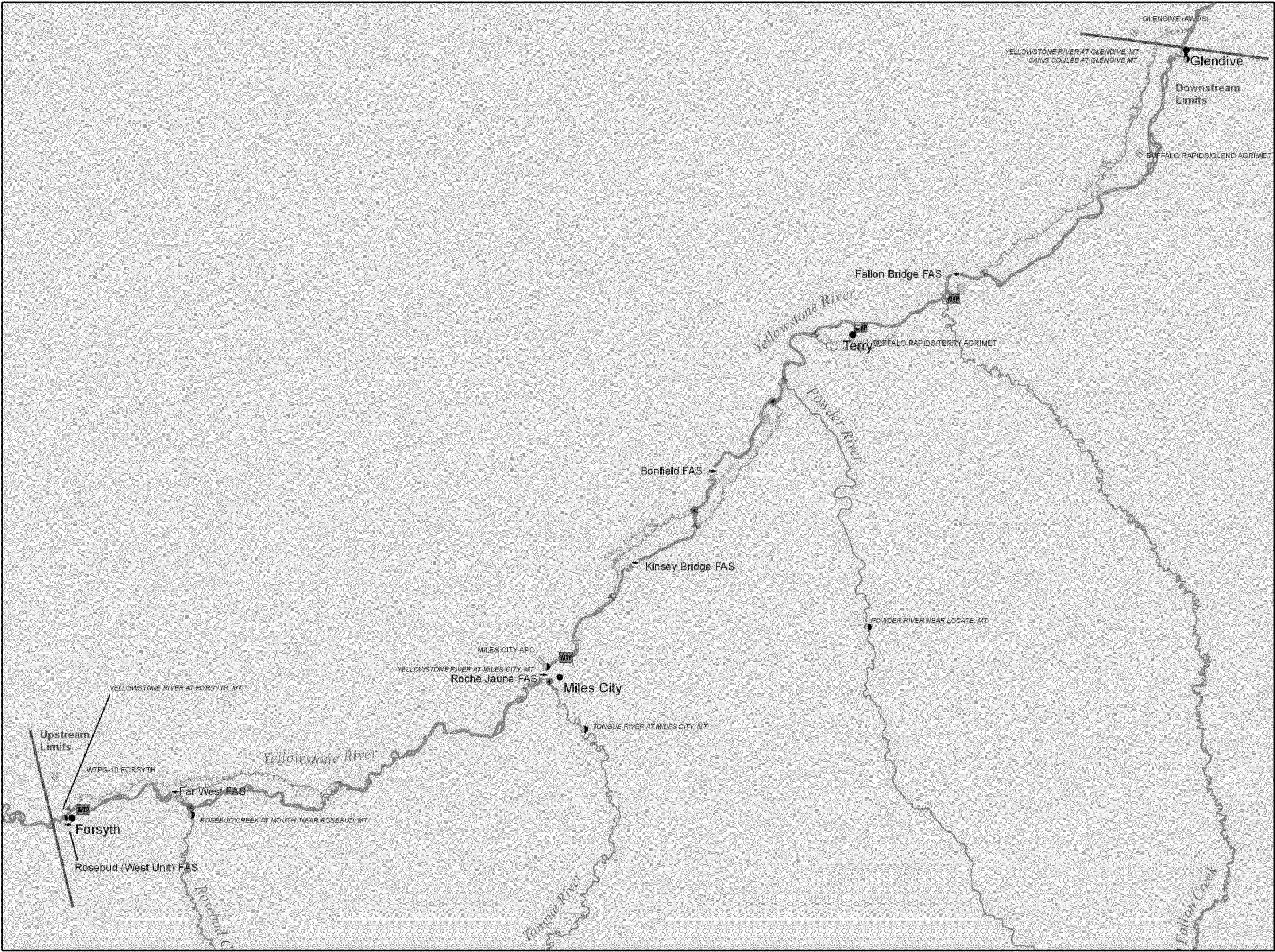
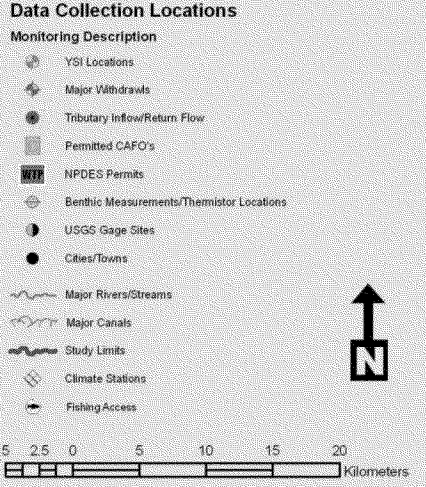
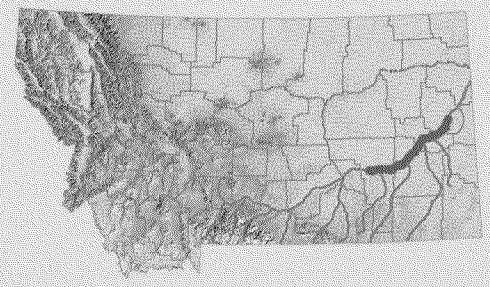


Figure 3.1. Yellowstone River QUAL2K Monitoring Locations



Yellowstone River Project Vicinity



Depth-and-width integrated sampling is planned to be coincident with the YSI locations (as well as for major tributaries and the comparison site), and is designed to bracket water quality and other measured parameters at the upstream and downstream ends of each of the seven subreaches. Based on a review of USGS gage sites, DEQ has concluded that only two natural tributaries in the modeling study reach will require monitoring during the—low flow— monitoring period; the Tongue and Powder River. However, any major tributaries that are flowing near their mouths during the synoptic sampling runs (e.g., O'Fallon or Rosebud creeks) will be sampled opportunistically. And because of their likely influence on water quality, several irrigation canals will be sampled. The Cartersville, Kinsey, Shirley, Terry Main and Main canals will be monitored for water withdrawal volume at their upper limits. They will also be sampled for quality/quantity at their confluence (inflows) with the river, when identifiable return points exist, to establish the influence of their return flow. In some cases (e.g., Bonfield FAS, Pirogue Island State Park, Terry Bridge etc.), monitoring sites will also be near the middle of a subreach. Benthic/rate measurements will be completed at these locations along with instantaneous water quality to provide a check to assure no major water quality changes have occurred within the subreach.

Water sample and other data will be collected during two 8-10 day periods in August and September 2007, for the purpose of establishing calibration and validation datasets for the simulated water quality state variables. This split-sample calibration-validation approach is appropriate for a Level 1 confirmation in which the model is tested using different meteorological and boundary conditions from which it was calibrated (Chapra, 2003). This—low-flow— period is considered representative of the critical limiting period where conditions of nuisance algae and/or low dissolved oxygen would limit beneficial uses in the Yellowstone River.

Mills et al. (1986) recommended that sampling occur at points where water quality standards may be violated, in addition to boundary conditions and key tributary breaks. Benthic measurements are planned for downstream of Forsyth, Miles City and Terry, to observe potential responses of the river to WWTP inputs. This has been initiated due to the fact that midday DO concentrations were measured below 5 mg/L during the 2006 field visit (Appendix A) in Miles City, and heavy nuisance algal growth was observed near Miles City at the Roche Jaune FAS.

Other important forcing data necessary for modeling include point source discharges, diffuse sources (non-point), and meteorological data. Municipal permitted point source discharges are located at Forsyth, Miles City, Terry, and near the border of Fallon/Prairie County. Nutrient and other data collected as part of the MPDES permits from point sources will be gathered from the DEQ Permitting and Compliance Bureau. If these are not deemed appropriate for modeling purposes, an additional effort will be made to organize a data collection effort at these point sources over the monitoring period. Non-point source data (e.g. groundwater monitoring) will not be collected as part of this project. Rather, the Montana Bureau of Mines and Geology (MBMG) GWIC database will be consulted to establish quality constituents of groundwater accretion. A cursory review of this database revealed a number of groundwater water-quality sampling locations in Rosebud, Custer, Prairie and Dawson counties.

Meteorological data are being collected at a number of stations independent from this study. Communities along the targeted reach such as Forsyth, Miles City, Glendive, etc. have NOAA or BOR weather stations that provide the necessary data for modeling. Those stations with hourly meteorological observations of either air temperature, wind speed, relative humidity, solar radiation or cloud cover are identified below (see also Figure 3.1):

1. Buffalo Rapids - Terry, MT (BRTM), BOR Agrimet
2. Buffalo Rapids - Glendive, MT (BRGM), BOR Agrimet
3. Glendive AWOS (WBAN 24087), NOAA
4. Miles City Municipal Airport (WBAN 24037, COOP ID 245690), NOAA
5. Forsyth W7PG-10 (AR184), NOAA

3.2.3 Sediment Oxygen Demand Measurements Using Benthic Chambers

Sediment Oxygen Demand in the Yellowstone River, August 2006. Sediment oxygen demand (SOD), or river-water oxygen consumption originating from the sediments, can be an important component of river DO dynamics (Bowman and Delfino, 1980; Matlock et al., 2003). We undertook SOD measurements at two locations in our targeted reach of the Yellowstone River in August 2006, using the sediment-core SOD method (Edberg and Hofsten, 1973). SOD was measured in paired, opaque core samples (Fig. 3.2) collected at the Roche Jaune FAS and the Fallon Bridge FAS. All SOD values were corrected for the water-column oxygen demand (WOD) of the water above the sediment cores (Suplee and Cotner, 1995). At the Roche Jaune FAS the WOD was undetectable, while SOD was (on average) $0.5 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$. However, the greatest proportion of DO demand was probably associated with thick beds of filamentous *Cladophora* at the site (we did not measure DO demand of the *Cladophora*, and no *Cladophora* was present on the sediment cores we collected). At the Fallon Bridge FAS, where no attached *Cladophora* was noted, WOD was $1.1 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$ and SOD was (on average) $0.7 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ (CV = 22%). SOD accounted for about 38% of the total DO demand in the river at the Fallon Bridge FAS, when WOD was integrated over the mean river water depth of 1 m.

From these preliminary measurements we concluded that SOD can be a major part of the river's DO dynamics, and should be directly measured for purposes of QUAL2K calibration and validation. Although QUAL2K calculates SOD based on diagenesis of settling organic carbon, temperature, etc., it also allows the user to input supplementary SOD if the model is underestimating measured SOD values (Chapra and Pelletier, 2003).

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Figure 3.2. Measurement of sediment oxygen demand in sediment core samples, Yellowstone River, August 2006. A. Paired sediment cores in their water bath, with YSI model 85 DO meters attached. The tube on the right only contained river water and was used to measure BOD. B. Close-up of the sealed sediment cores and attached YSI DO probes. The metal wires were attached to paddles used to stir the water above the sediments just prior to taking the DO measurements. Water bath temperature was maintained at the temperature measured in the river during sediment collection.

In Situ Measurement of SOD Using Benthic Chambers, Summer 2007. EPA indicates that *in situ* measurements of SOD are preferable to laboratory sediment-cores techniques (Mills et al., 1986). And although sediment cores were used for the August 2006 reconnaissance, it is also the

opinion of Suplee (of this QAPP) that *in situ* SOD methods should be used in 2007, based on past experience measuring SOD (see Suplee and Cotner, 1995; Suplee and Cotner, 2002; Cotner et al., 2004). This is because the bed of the Yellowstone River was comprised of coarse and fine gravel, making the collection of undisturbed sediment cores quite difficult. It is also difficult to simulate flow velocities across the sediments in a sediment core. Simulation of river velocity over the sediments is important to accurate measurement of river SOD (Hickey, 1988; Mackenthun and Stefan, 1998).

We intend to use *in situ* opaque SOD chambers similar in design to that of Hickey (1988; Fig 3.3). His chamber design is specialized for river use and can simulate *in situ* river velocities. Opaque chambers allow for simulation of nighttime SOD, which is the critical time period when river DO is the lowest and which is of most interest to us. A chamber volume/surface ratio (L/m^2) of < 100 generally provides good declines in DO over efficient time frames (2-12 hours), therefore a ratio of 70 will be used for our chambers. The chamber pump will simulate velocities across the sediment ranging from zero to 0.4 m sec^{-1} , which encompasses the range of near-bottom water velocities measured in the river in August 2006 (Appendix B). A flexible skirt of rubber or a similar inert material will be attached around the circumference of the chamber where it interfaces with the sediments. Due to the river bottom's composition, we will probably not be able to press the chambers in to the sediments very deeply, therefore the skirt will help provide an additional seal between the sediments and the enclosed water in the chamber.

Solute Fluxes to be Measured Using the In Situ Benthic Chambers. Di Toro et al. (1990) recommended that if SOD is being measured *in situ*, dissolved methane and ammonia should also be measured, and QUAL2K allows the user to prescribe these fluxes (Chapra and Pelletier, 2003). The flux of total dissolved inorganic carbon (DIC) will also be measured. The sediment DIC flux will be compared to the DO flux in order to calculate the respiratory quotient (RQ; CO_2 flux/ O_2 flux), which will show if organic material on the river bottom is being metabolized by largely aerobic or anaerobic processes (Wetzel, 1983; Suplee and Cotner, 2002). This information will be valuable for model calibration.

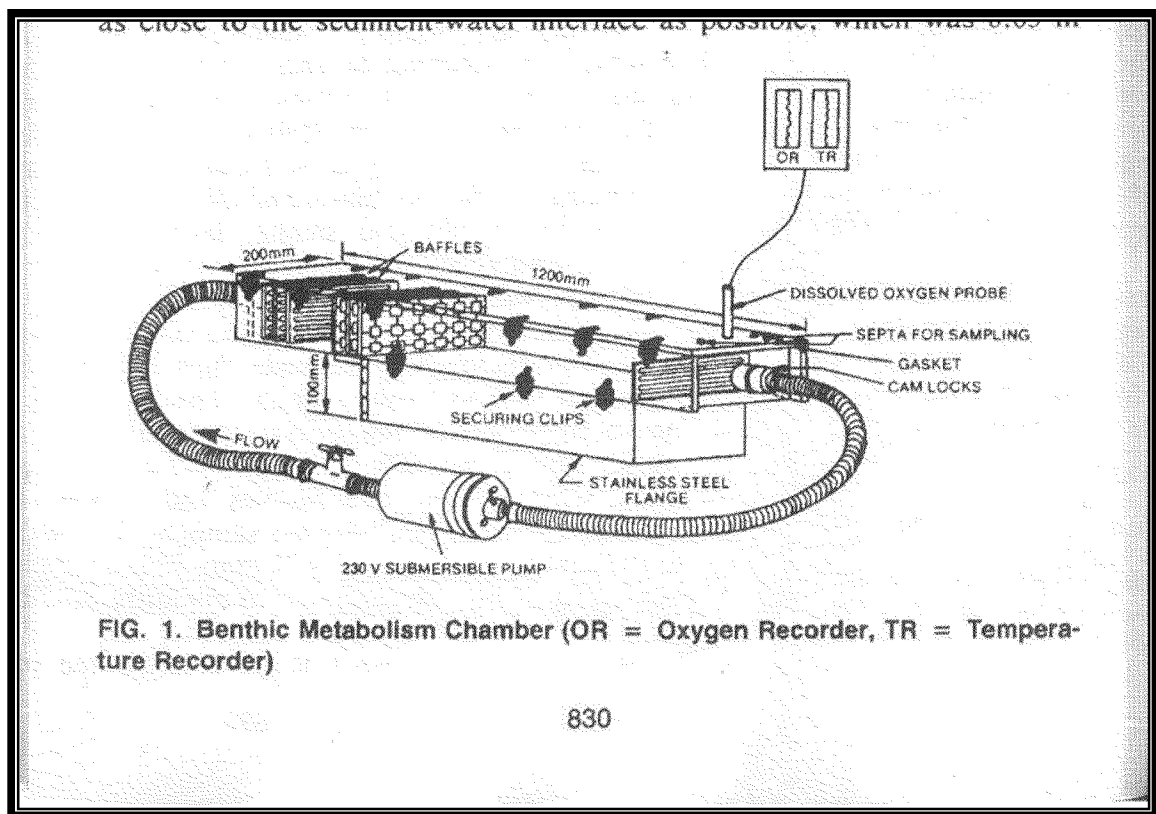


Figure 3.3. General diagram of the flow-adjustable SOD chamber proposed for use in the project, from Hickey (1988). The final design will be a modification of this basic layout. For example, a flexible skirt will be added around the circumference of the chamber to assure a good seal to the river bottom in cases where the device cannot be pressed very deeply in to the sediments.

3.2.4 Other Rate Measurements

QUAL2K allows the user to input maximum phytoplankton photosynthesis rates at a given temperature ($k_{gp}[T]$; Chapra and Pelletier, 2003). These will be measured directly, methods for which are outlined in the SAP. Simulated night-time DO uptake by *Cladophora spp.* will be measured at locations (e.g., Miles City) where dense beds are present and likely influence DO dynamics.

3.2.5 Other Benthic Measurements

Estimate of Algal Growth Cover and Proportion of Applicable Channel SOD. The % river bottom cover by algae and the % river bottom to which SOD measurements apply will be estimated at cross sections of specified sites. Both of these parameters can be prescribed by the user in QUAL2K. During the transect collection of benthic algae, a record will be made at each sampling locale indicating the degree and type of algae coverage. QUAL2K also allows the user to dictate the proportion of river bottom that SOD measurements apply towards, under the assumption that only a proportion of the river bottom is capable of generating a significant SOD.

We will estimate in the field the proportion of the river bottom along the transect that has velocity and depth characteristics similar to the sites where SOD was measured. Our assumption is that areas of high velocity and scouring (e.g., river thalweg) will have lower SOD than the slower, more depositional parts of the river, where SOD measurements will be made. The model will be setup to reflect the values provided by these field-collected coverage estimations.

3.2.6. Water Column Measurements

Most water quality measurements are routine and are adequately detailed in the SAP or existing DEQ QAPPs (e.g., DEQ 2005). However, some non-standard analytical measurements are important to QUAL2K operation and will therefore be completed. QUAL2K prompts the user for the stoichiometry (C:N:P ratio) and mass of suspended organic matter (—seston||; living and detrital organic material), so samples for these will be collected and analyzed. See the SAP for details on sample collection procedures.

Real-time measurements (30 min increments) using YSI 6600 EDS sondes will be recorded at 8 sites, for up to 45 continuous days of monitoring. There are currently no DEQ SOPs for using these instruments in long-term deployment. Therefore, data quality objectives for their use are detailed in Section 4.0.

3.2.7 Meteorological Measurements

According to Troxler and Thackston (1975) and Bartholow (1989), it is possible that the meteorological data collected at airports or in towns on the bluffs above the Yellowstone River by NOAA/BOR may not be representative of conditions at the river. Therefore, an independent weather station unit will be installed by DEQ on a small island in the river within the Fort Keogh Agricultural Experiment Station, near Miles City and its airport weather station. If there are significant differences between the on-river and official Miles City NOAA weather data, the differences can be used to help adjust other official data on other parts of the modeling reaches. An adjustment procedure (Raphael, 1962; Bartholow, 1989) will be based on the assumption that the rest of the Yellowstone study area is fairly homogenous with respect to elevation, aspect and land use.

3.2.8 Hydraulic Measurements

Water-quality models are typically no better than required data (i.e., coefficients), especially the travel time used in their mass transport formulation (Hubbard et al., 1982; Wilson et al., 1986; Barnwell et al., 2004). Accurate representation of model hydraulics is necessary to achieve the model output quality desired for this study (see section 7.3, Model Usability). Several approaches have been proposed for estimation of hydraulic properties used in QUAL2K. Paschal and Mueller (1991) and Ning et al. (2000) utilized velocity measurements in a number of modeling reaches to estimate travel time. Kuhn (1991) and Bilhimer et al. (2006) introduced a dye tracer and used florescence measurements to identify travel time between modeled reaches. Park and Lee (2002) used a formulation of Manning's equation and assume prismatic trapezoidal channel geometry. DEQ will directly measure channel geometry, velocity, and associated

roughness coefficients at specified sites. Height and width of the lowhead dam near Forsyth will be obtained for calculation of re-aeration and associated hydraulics.

Preliminary calculation of travel time between Forsyth and Glendive has already been completed using a Microsoft VBA program developed by USGS for the Yellowstone River (McCarthy, 2006). The USGS software indicated a travel time of 2.25 days, which is based on the observed flood wave celerity of two storm events and the ratio of this velocity to most probable base flow velocity. McCarthy (2006) is quick to point out that this estimate could easily be off by a factor of two. A dye tracer study is planned to be completed through the USGS in summer 2008 for validation of computed travel time.

4.0 Quality Objectives and Criteria

4.1. Quality Criteria for Benthic Chamber SOD

In spite of its importance to DO dynamics, SOD measurement is not found in Standard Methods (APHA, 1998); however, there is a significant body of literature on the topic (see review by Bowman and Delfino, 1980). Bowman and Delfino (1980) defined 3 criteria for acceptable SOD measurements: (1) consistency; (2) reproducibility; and (3) efficiency. Consistency refers to the ability of the investigator to adhere to the prescribed SOD measuring technique. Consistency will be addressed by adherence to the techniques outlined in the SAP. Reproducibility addresses replicate variability. We will measure SOD in duplicate chambers at each site, with a CV target of $\pm 20\%$, which is considered good (Bowman and Delfino, 1980). WOD (used to correct gross SOD) will be measured via the Winkler method in triplicate 300 ml dark bottles incubated at ambient river temperatures. Efficiency refers to the ability to make a sufficient number of measurements over a relatively short time period. We intend to be able to complete each set of SOD measurements within 2-8 hours of initiation, by assuring that the chambers have a chamber volume/sediment surface ratio of 70. If the longer timeframe (i.e. 8 hrs) is needed, these will be run overnight so that SOD measurement will not consume the working hours required to complete other project tasks.

4.2. Quality Criteria for YSI 6600 EDS Sondes Deployed Long-Term

Long Term Deployment of YSI 6600 EDS Sondes. YSI 6600 EDS sondes will be deployed along the river and continuously record data for up to 45 days. Each instrument will be calibrated in the laboratory prior to deployment, and checked again for instrument drift upon retrieval. The Alliance for Coastal Technologies (ACT) is a third-party organization that carries out performance verification studies for these (and other) instruments in rigorous, long-term field deployments around the U.S. (see reports and organization information at: http://www.act-us.info/evaluation_reports.php) We have used their—Performance Verification Statement|| reports to develop quality criteria for the sondes that we will deploy on the Yellowstone River. These ACT reports discuss, on a probe-type by probe-type basis, the period of time until biofouling begins to interfere with instrument measurements. Days-to-interference from biofouling vary, but typically fall in the range of 14-35 days; in some cases, however, no interference is noted even after 44 days of continuous deployment (ACT, 2007). To assure quality measurements, the YSI sondes will be checked for biofouling in our study at the

approximate midpoint of the study, 25-30 days after initial deployment, and cleaned and recalibrated as needed. Data collected to that point will be down loaded to a laptop for safe keeping.

Instrument drift during the deployment period is an equally important issue, and is addressed below, by measurement type.

Dissolved Oxygen. Accurate DO measurement is key to this study, so DEQ has purchased YSI's ROX™ optical DO sensors. These sensors became available from YSI in 2006 and in testing show no significant drift over 1-2 month deployment timeframes during which they were tested (YSI, 2007). This is a great improvement over the drift observed for YSI's polarographic probes (ACT, 2004). The quality criterion for DO concentration data collected over the sampling period using ROX™ optical sensors is that instrument drift will be ≤ 0.2 mg DO/L, using the single-point, water-saturated air technique.

Turbidity. In an ACT test at 7 sites around the country with deployment times ranging from 29-77 days, instrument drift (5 NTU, initial standard calibration) ranged from 0-17%, with a mean drift of 8% (ACT, 2007). The quality criterion for turbidity data collected over the sampling period in our study is that instrument drift, from initial calibration at 11.2 NTU, will be $\leq 10\%$ (YSI has calibration solution of 11.2 NTU which is as close to the 5 NTU as they provide).

*Chlorophyll *a*.* In another ACT test at 5 of the 7 sites mentioned above, Chl *a* (using Rhodamine WT as the initial calibration dye) drift during deployment ranged from 31-63%—pre-cleaning|| of the probe, and from 0.8 to 18% (mean 7%)—post-cleaning|| of the probe (ACT, 2006). (Keeping this probe clean clearly diminishes drift.) The quality criterion for Chl *a* data collected over the sampling period in our study is that instrument drift from calibration (using Rhodamine WT) will be $\leq 10\%$, post-cleaning.

4.3. Quality Criteria for Other Field Measurements

Routine Water Quality Measurements. All quality assurance and quality control (QA/QC) requirements followed by DEQ will be instituted for this project. This includes use of standard site visit forms and chain of custody forms for all samples. The QA/QC requirements for water quality samples, flow measurements, etc. are described in detail in DEQ (2005), and are sufficiently covered that repeating them here is not needed.

Dye Tracer Study. The dye tracer study, if initiated, will be carried out by the USGS and all QA/QC procedures developed and implemented by that agency will be followed.

5.0. Assessment and Response Actions

The QA program under which this project operates includes independent checks obtained for sampling and analysis (i.e., laboratory quality assurance processes). The DEQ QA officer may perform audits of field operations and laboratory activities during the course of the project. The QA officer has the authority to stop work on the project if problems affecting data quality that will require extensive effort to resolve are identified.

Any changes to the SAP which may result after the project is initiated will be documented and included as an addendum to the SAP. Project responsibilities for individuals directly involved in the project are shown in Table 5.1 below. The project manager (Suplee) will communicate all significant changes in field protocols or sampling locations to the modeling staff and the DEQ QA officer, as they arise. The likely impacts of these changes on project success will be discussed on a case-by-case basis, and the project adjusted/modified to continue to meet the objectives in this QAPP, as needed.

Table 5.1. Project Personnel Responsibilities.

Name	Organization	Project Responsibilities
Michael Suplee	MT DEQ	Project Management/data collection
Kyle Flynn	MT DEQ	Model Calibration and Validation
Michael Van Liew	MT DEQ	Model Calibration and Validation
Monitoring Staff 1	MT DEQ	Data Collection
Monitoring Staff 2	MT DEQ	Data Collection

6.0 Data Review, Validation and Verification

6.1 Modeling Analyses - Preliminary Data Compilation and Review

Prior to data use, DEQ will compile all information in a usable format for modeling. The necessary QC will be completed to ensure that DEQ monitoring efforts, as well as ancillary data sources used in the modeling effort (i.e., other agencies), are suitable for modeling purposes. USGS, BOR, and NOAA data (streamflow and weather) will be downloaded from each agency's web site and assembled into individual data files. These data will be reviewed by DEQ for quality factors such as completeness, accuracy, precision, comparability, and representativeness (DEQ, 2005). The same will be done for DEQ data. The appropriate conversions will be made, and time-series data will be generated in a format suitable for modeling (e.g., QUAL2K operates in SI units and on an hourly time step [Chapra, 2003]). Additional data aggregation is necessary given the steady-state limitations of the modeling framework. Model boundary conditions such as streamflow and meteorology are allowed to vary diurnally in the model, however they are considered constant for the length of the simulation period. Therefore a reach having a three day travel-time is exposed to three days of different hourly meteorological forcings which must be averaged to achieve representative input data (e.g., by taking the three day average of the 7:00-8:00 a.m. air temperature, 8:00-9:00 a.m. temperature, etc.). This procedure is necessary for all meteorological input (air temperature, wind speed, dewpoint, etc.) and any other water quality constituent that needs to be analyzed diurnally (temperature, DO, nutrient speciation, etc.). Point-source water quality data are allowed to vary sinusoidally based on a specified mean,

range, and time of maximum. Associated discharges are considered steady-state for the entire simulation period.

7.0 Validation and Verification Methods

7.1 QUAL2K Model Calibration and Validation

Calibration has become increasingly important with the need for valid and defensible models for TMDL development (Donigian and Huber, 1991; Little and Williams, 1992; Wells, 2005; DEQ, 2006b). Model calibration defines the procedures whereby the difference between the predicted and observed values of the model are brought to within an acceptable range by adjustment of uncertain parameters. Ideally, this is an iterative process whereby deficiencies in the initial parameterization are reviewed in a feedback loop to reformulate and refine the calibration. General information related to model calibration criteria and validation considerations can be found in Thomann (1982); James and Burges (1982); Donigian (1982); ASTM (1984); and Wells (2005). For the purpose of this QAPP (and subsequent modeling efforts) two tests will be utilized to define the sufficiency of the model calibration. These are percent bias and the sum of the squared residuals.

Percent Bias. Percent bias is defined as the consistent or systematic deviation of results from the "true" value (Moore and McCape, 1993) and can be a result of a number of deficiencies in modeling. These include: (1) incorrect estimation of model parameters, (2) erroneous observed model input data, (3) deficiencies in model structure or forcing functions, or (4) error of numerical solution methods (Donigian and Huber, 1991). Percent bias is calculated as the difference between an observed (true) and predicted value as shown below.

$$\%B = \frac{OBS_i - PRED_i}{OBS_i} \quad (1)$$

Where:

- B = Percent Bias
- OBS_i = Observed State Variable
- SIM_i = Simulated State Variable

Percent bias will be computed for each calibration location (7 different points in the modeling reach) to evaluate the efficiency of the QUAL2K Yellowstone model. Overall percent bias should approach zero.

Sum of Squared Residuals (SSQ). SSQ is a commonly used objective function for water quality model calibration (Little and Williams, 1992; Chapra, 1997). It compares the difference between the modeled and observed ordinates, and uses the squared differences as the measure of fit. Thus a difference of 10 units between the predicted and observed values is one hundred times worse than a difference of 1 unit. Squaring the differences also treats both overestimates and underestimates by the model as undesirable. The equation for calculation of the sum of least squares is shown below (Diskin and Simon, 1977). SSQ will be used as a criterion for overall

model evaluation and will be calculated as the summation of all squared residuals for the seven calibration/validation nodes in the model, as well as for the individual nodes.

$$\text{Minimize } Z = \sum_{i=1}^{i_n} [OBS_i - PRED_i]^2 \quad (2)$$

Where:

Z = Sum of Least Squares

Model Validation. Validation is defined as the comparison of modeled results with independently derived numerical observations from the simulated environment. The same statistical procedures identified in model calibration will be implemented to the validation dataset. Model validation is, in reality, an extension of the calibration process (Reckow, 2003; Wells, 2005) and is often referred to as confirmation. Its purpose is to assure that the calibrated model properly assesses the range of variables and conditions that are expected within the simulation. Although there are several approaches to validating a model, perhaps the most effective procedure is to use only a portion of the available record of observed values for calibration and the other for validation (Chapra, 1997). This type of split-sample calibration-validation is proposed for the Yellowstone River modeling project. Two periods of representative warm-weather conditions will be evaluated; a calibration period in August 2007, and a validation period in September 2007.

7.2 Model Sensitivity

Sensitivity analysis is a technique that can greatly enhance the model calibration process (Chapra, 2003). It guides the modeler to focus the calibration on the most sensitive model parameters and allows the user to judge the relative magnitude of various model parameters on key state variables. Sensitivity is typically expressed as a normalized sensitivity coefficient (Brown and Barnwell, 1987) in which the percent change in the model input parameter is compared to the change in model output. The equation for calculating the sensitivity of a model parameter is shown below:

$$\text{Normalized Sensitivity Coefficient (NSC)} = \frac{Y_o / Y_o}{X_i / X_i} \quad (3)$$

Where:

ΔY_o = Change in the output variable Y_o

ΔX_i = Change in the input variable X_i

Sensitivity analysis is often accomplished using a one-variable-at-a-time perturbation approach (Brown and Barnwell, 1987; Chapra, 1997). A summary of the normalized sensitivity coefficient (NSC) calculated for the one-variable-at-a-time approach will be included as part of

the reporting which will include the parameter modified, the range and increment of modification (e.g. $\pm 10\%$), percent change in the modeling results, and the calculated NSC. The literature will also be consulted to assess modeling efforts similar in nature to ours (e.g, Paschal and Mueller, 1991; Reckow, 1994; Drolc and Koncan, 1999). More complex computational algorithms are also available, such as first-order error analyses and Monte Carlo simulation. An older version of QUAL2K, QUAL2E-UNCAS offers this functionality. Unfortunately, deficiencies in the benthic algae component of this older model make it less useful (Park and Lee, 2002). DEQ will assess the utility of QUAL2E-UNCAS at a later date, although we have no plans to use it for the Yellowstone River project.

Research has shown that sensitivity analyses by themselves are not adequate for characterizing model uncertainty (Melching and Yoon, 1996). Reckow (1994 & 2003) and Chapra (2003) indicated uncertainty analyses should be considered as a routine part of ecological modeling studies. Uncertainty stems from the lack of knowledge regarding model input parameters (Melching and Yoon, 1996) and the processes the model attempts to describe (Beard, 1994). Potential sources of uncertainty in the Yellowstone QUAL2K model have been identified *a priori* by DEQ and include the following:

- (1) Estimation of uncertain model parameters
- (2) Uncertainty in observed model input data
- (3) Deficiencies in model structure and forcing functions
- (4) Mathematic errors in numerical methods

Chapra (2003) indicated that modeling uncertainty is best expressed probabilistically. This is even more critical for this effort since numeric nutrient criteria are being developed. A simplified Monte Carlo approach to address uncertainty analysis is proposed for the Yellowstone QUAL2K modeling, in order to account for the combined effect of parameter sensitivity and parameter uncertainty (i.e., a highly sensitive parameter that is fairly certain can have much less effect on the uncertainty of model output than a much less sensitive parameter that is highly uncertain). Probability density functions (PDFs) will be estimated for model parameters using either the uniform, normal, or triangular distributions identified in Chapra (1997) enabling a confidence interval to be calculated from state variable output. This will provide statistical measure of significance on model prediction uncertainty. The Monte Carlo approach is fully described in Brown and Barnwell (1987) and Chapra (1997). It is unclear at this time whether DEQ will attempt to use the older version of QUAL2E-UNCAS for this analyses. It is proposed to be done manually at this time (using only a handful of the most sensitive model parameters).

7.3 Model Usability

Acceptance of Modeling Results. QUAL2K has been shown to be a reliable tool for the prediction of water quality when the conditions in the river are similar to those used to calibrate and validate the model (Drolc and Koncan, 1996). The acceptance of the QUAL2K model will be gauged by DEQ in several ways, including: (1) review of the—goodness of fit—indices described previously, (2) comparison of simulated and observed values against *a priori*, user-specified criteria, and (3) model testing. User specific criteria developed by DEQ for the overall Yellowstone River QUAL2K model are shown in Table 7.1.

Table 7.1. Preliminary Calibration and Validation Criteria for Yellowstone QUAL2K model.

State Variable ⁽¹⁾	Criteria in Percent	Unit Criteria
Temperature	±5%	±1 °C
Dissolved Oxygen	±10%	±0.5 mg/L
Bottom Algae	±20%	mg/m ²
Chlorophyll a	±10%	µg Chl a /L

⁽¹⁾ *Should meet the minimum of percent or unit criteria*

Model validation testing will be completed per Reckow (2003). Three levels of validation testing are available, although only one is proposed. Level 0 testing involves validation of the model over a period that is almost identical to that of the calibration period. Level 1 testing involves the use of a different meteorology for the calibration and validation runs. Level 2 involves the use of both different meteorology and point source loadings. The Level 1 approach is proposed for the Yellowstone River Project given the fact that numeric nutrient criteria are being developed only for a specified flow regime (e.g. low flow). The credibility of these criteria will hinge on the confidence in the model predictions and the understanding of the associated sensitivity and uncertainty in model parameters.

N and P concentrations indicated by the final model as potential criteria will be compared to the N and P concentrations collected during the same period at the comparison site, and to literature values from empirical nutrient-Chl *a* models. If results of all 3 are within an order of magnitude of each other, the results from the model will be considered reasonable due to the site specific nature of the results and documentation of the calibration-validation procedures. We anticipate that concentrations provided by the upstream comparison site will be lower than the output from the model, given that the comparison site has less turbid, colder water. Modeled results that differ from the comparison site/empirical models by more than an order of magnitude will result in a careful re-analysis of the model input parameters. If after the re-evaluation the results from the mechanistic model still differ considerably from the other two approaches, DEQ will indicate this in the final report and provide discussion as to the likely reasons why, and also provide recommendations as to whether or not the model is an appropriate tool for developing numeric nutrient criteria, and why.

8.0 Special Training/Certification

All project participants will have completed a First Responder first-aid course, and also be certified in CPR. All participants who will work on the boat will have completed a U.S. Coast Guard certification course in 'Boating Skills and Seamanship'. All individuals who will be using the boat on the Yellowstone River will, prior to beginning work on the Yellowstone River, undertake at least one day of boat-use practice at Hauser Reservoir near Helena, MT.

9.0 Documents and Records

Data generated during this project will be stored on field forms, in laboratory reports obtained from the laboratories and in Excel spreadsheets hosted by DEQ shared network servers (backed up on a daily basis). Site Visit/Chain of Custody forms will be properly completed for all samples. Written field notes, field forms (photo log, site information), and digital photos will be processed by DEQ staff following QA/QC procedures to screen for data entry errors. Data provided by the State Lab and the Flathead Lake Biological Station will be in a SIM-compatible format, and will be readied for import into the DEQ's local STORET database and EPA STORET database by the Montana Department of Environmental Quality. Data will be processed with Excel and with Minitab release 14. ArcView version 9 ArcMap will be used for GIS applications. The GPS coordinate system datum will be NAD 1983 State Plane Montana, in decimal degrees, to at least the fourth decimal. All data generated during this project will be available to the public.

A technical report document will describe the findings of the study and will accompany the QUAL2K model developed for the project. The report will summarize the approaches taken (i.e., this QAPP and the SAP), the results of the model calibration & validation, sensitivity analysis and uncertainty analysis. The nitrogen and phosphorus criteria derived from the model will be compared to literature values and to data from the upstream quasi-reference site, and will be thoroughly discussed in the report. Recommendations will be made in the report as to whether or not the mechanistic modeling approach appears to be a reasonable and useful method.

10.0 Schedule for Completion

Assuming full funding is received, equipment purchases will proceed in late 2006 and spring 2007. Coast Guard boating safety and first aid/CPR courses will be completed either in spring or early summer, 2007. The YSI sondes will be deployed at the first reasonable opportunity when the river begins to approach base flow, probably sometime in late July or early August. Synoptic sampling will occur as two separate events, in August and September 2007, preferably about 20-30 days apart. Water quality and other data should be ready for use by November 2007, at which point the model calibration and validation can begin. The model and its associated report should be completed by May 2008.

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11.0 Project Budget

Table 11.1. Projected Budget for Purchases Required to Complete Project						
Item*	#	Vendor	Catalog #	Unit Price	Total	Probable \$ Source
Infrastructure Purchases						
16' mod-V Jon boat w/ outlocks, trailer, clean 2-stroke Evinrude 90 hp Outboard jet.	1	Local		\$13,906.00	\$13,906.00	Monitoring Section
Large Sea Anchor	1	Local		\$100.00	\$100.00	Monitoring Section
Garelick Boat Hook 3.5-8 ft	1	Cabelas	IG-016883	\$24.99	\$24.99	Monitoring Section
Variable 24" boom, 200 lb cap. Winch/Depth Meter (43 lbs)	1	WILDCO	85-E20	\$1,449.00	\$1,449.00	Monitoring Section
WeatherHawk Weather Station	1	Ben Meadows	6JF-111372	\$1,395.00	\$1,395.00	Data Management Section
Honda 1500 Watt 240/120/12 V gasoline generator	1	Local	QT-522130	\$650.00	\$650.00	Monitoring Section
Lab oven to 200° C	1	Fisher	13-254-29	\$894.29	\$894.29	Monitoring Section
US DH-95 (29 lb) "Clean" Depth Integrating Sampler [†]	1	Ricky Hydro	401-055	\$2,100.00	\$2,100.00	Monitoring Section
†This is the "clean" model, also suitable for metals and pesticides sampling. The bronze DH-59 model (\$725.00) may be adequate for nutrients.				Total:	\$20,719.28	
Project-Specific Purchases (Equipment)						
SOD Chamber	2	A. R. I.	Custom	\$950.00	\$1,900.00	Monitoring Section
SOD chamber 12 v power supply & submersible pump	2	Various	Custom	\$645.00	\$1,290.00	Monitoring Section
Sonde Deployment Apparatus	8	A. R. I.	Custom	\$335.00	\$2,680.00	Monitoring Section
1/8" Stainless Steel Cable	1200	Ricky Hydro	106-073	\$0.30	\$360.00	Monitoring Section
Heavy Duty cable cutter	1	Ricky Hydro	106-186	\$97.00	\$97.00	Monitoring Section
Multi-cavity Swage Tool	1	Ricky Hydro	106-185	\$145.00	\$145.00	Monitoring Section
Stirrer Plate	1	Fisher	14-493-120S	\$160.14	\$160.14	Monitoring Section
Teflon Stirrer bar assortment	1	Fisher	14-511-59	\$63.32	\$63.32	Monitoring Section
50 ml buret for Winkler titration	1	Fisher	03-765	\$135.30	\$135.30	Monitoring Section
100 ml volumetric pipette	2	Fisher	13-650-2U	\$23.98	\$47.96	Monitoring Section
Rubber safety pipet filler bulb	1	Fisher	13-681-51	\$22.81	\$22.81	Monitoring Section
4 X 6 ring stand	1	Fisher	14-670A	\$31.15	\$31.15	Monitoring Section
Buret clamp	1	Fisher	05-779	\$36.79	\$36.79	Monitoring Section
Clamp for YSI sonde (3.5" grip)	1	Fisher	05-769-8	\$27.68	\$27.68	Monitoring Section
250 ml Erlenmeyer flasks (case of 6)	1	Fisher	10-041-4B	\$96.75	\$96.75	Monitoring Section
Wheaton 300 ml BOD bottle (case of 24)	1	Fisher	02-926-27	\$217.11	\$217.11	Monitoring Section
Wheaton 300 ml Dark BOD bottle (case of 20)	1	Fisher	02-926-89	\$288.12	\$288.12	Monitoring Section
Wheaton Dark BOD bottle caps (case of 50)	1	Fisher	02-926-7	\$31.94	\$31.94	Monitoring Section
Wheaton 12-place BOD bottle holder rack	2	Fisher	02-663-103	\$30.98	\$61.96	Monitoring Section
3-place FisherBrand PVC Vacuum manifold w/ 1/4 in barb	1	Fisher	09-753-39A	\$595.43	\$595.43	Monitoring Section
47 mm Nalge vacuum filter holder	3	Fisher	09-747	\$117.79	\$353.37	Monitoring Section
120 v high-capacity vacuum pump w/ gauges & regulators, 1/4 in	1	Cole-Parmer	C-07061-40	\$369.00	\$369.00	Monitoring Section
5.25 gallon Nalgene carboy with built in pour spout	2	Fisher	02-923-15C	\$71.71	\$143.42	Monitoring Section
Gasoline for boat, generator	60			\$3.00	\$180.00	Monitoring Section
Misc.	1			\$1,000.00	\$1,000.00	Monitoring Section
Chemical Supplies						
Alkaline Iodide Azide Reagent (500 ml)	1	Fisher	LC10670-1	\$31.13	\$31.13	Monitoring Section
Manganese Sulfate Solution (500 ml)	1	Fisher	SM20-500	\$29.92	\$29.92	Monitoring Section
Concentrated Sulfuric Acid (2.5 L)	1	Fisher	A484-212	\$68.75	\$68.75	Monitoring Section
Starch indicator, 1%, with salicylic acid preservative	1	State Lab				Monitoring Section
0.01 N Sodium thiosulfate solution (1 L)	1	Fisher	LC25000-2	\$17.63	\$17.63	Monitoring Section
1 L Rhodamine WT 20% dye solution (sold in 1 gallon jugs)	1	Fisher	NC9250029	\$305.00	\$305.00	Data Management Section
				Total:	\$10,786.63	
Laboratory Analytical Costs (includes reps and blanks)[†]						
<i>Water nutrients, Chl a, seston: 14 sites X 2 (Aug, Sep) X 5% replication, + 14 blanks</i>						
TN	44	FLBS		\$13.37	\$588.28	Standards Section
TP	44	FLBS		\$13.37	\$588.28	Standards Section
DON	44	FLBS		\$14.37	\$632.28	Standards Section
NO2/3	44	FLBS		\$12.11	\$532.84	Standards Section
Ammonia	44	FLBS		\$12.44	\$547.36	Standards Section
DOP	44	FLBS		\$14.37	\$632.28	Standards Section
SRP	44	FLBS		\$12.00	\$528.00	Standards Section
TIC	44	FLBS		\$14.68	\$645.92	Standards Section
TSS	44	State Lab		\$9.20	\$404.80	Standards Section
Turbidity	44	State Lab		\$6.90	\$303.60	Standards Section
Benthic Chl a	154	State Lab		\$25.00	\$3,850.00	Standards Section
Phytoplankton Chla	44	FLBS		\$15.41	\$678.04	Standards Section
Phyto AFDW	44	FLBS		\$6.00	\$264.00	Standards Section
Seston total C	44	FLBS		\$6.00	\$264.00	Standards Section
Seston total N	44	FLBS		\$6.00	\$264.00	Standards Section
Seston total P	44	FLBS		\$6.00	\$264.00	Standards Section
Ammonia (Chmbrs): 3 chmbrs/site X 2 (start, finish) X 7 sites X 2 (Aug, Sep), + 7 blanks	91	FLBS		\$12.44	\$1,132.04	Standards Section
DIC (Chmbrs): 3 chmbrs/site X 2 (start, finish) X 7 sites X 2 (Aug, Sep), + 7 blanks	91	FLBS		\$14.68	\$1,335.88	Standards Section
				Total:	\$13,455.60	
				Grand Total:	\$44,961.56	

[†] FLBS prices are as-quoted. There may be a 1.41 multiplier added to each cost if the UM overhead costs apply to each analysis.

12.0 References

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Appendix A

DATA COLLECTED ON THE YELLOWSTONE RIVER, AUG. 2006

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Site Name, Elevation (ft)	Distance From Shore	Site Depth	Temperature (°C)	DO (mg/L)	DO (% SAT)	Saturation	Notes
Far West FAS (frm L. bank)	1 m	< 50 cm	25	7.2	96	[DO SAT = 7.5 mg/L]	Bottom
(2480 ft)	3 m	75 cm	23.9	8.9	116	[DO SAT = 7.7 mg/L]	Bottom
8/14/2006, 6:35 PM	6 m	75 cm	23.9	9.3	121	[DO SAT = 7.7 mg/L]	Bottom
	9 m	1 m	23.9	9.3	121	[DO SAT = 7.7 mg/L]	Bottom
	12m	1.1 m	24	9.5	123	[DO SAT = 7.7 mg/L]	Bottom
Kinsey Bridge FAS (frm L. bank)	2 m	35 cm	26.4	8.2	109	[DO SAT = 7.5 mg/L]	
(2326 ft)	10 m	45 cm	24.5	8.4	111	[DO SAT = 7.6 mg/L]	Bottom
8/15/2006, 12:10 PM	10 m	0 cm	24.5	8.5	112	[DO SAT = 7.6 mg/L]	Surface
	20 m	55 cm	24.2	8.4	109	[DO SAT = 7.7 mg/L]	Bottom
	20 m	0 cm	24.2	8.4	109	[DO SAT = 7.7 mg/L]	Surface
	30 m	55 cm	24.2	7.9	103	[DO SAT = 7.7 mg/L]	Bottom
	30 m	0 cm	24.2	8.4	109	[DO SAT = 7.7 mg/L]	Surface
	40 m	38 cm	24.2	8.3	108	[DO SAT = 7.7 mg/L]	Bottom
	40 m	0 cm	24.2	8.4	109	[DO SAT = 7.7 mg/L]	Surface
	70 m	45 cm	24.2	8.5	110	[DO SAT = 7.7 mg/L]	Bottom
	70 m	0 cm	24.1	8.5	110	[DO SAT = 7.7 mg/L]	Surface
	77 m	90 cm	24	8.0	104	[DO SAT = 7.7 mg/L]	Bottom
	77 m	0 cm	24	8.4	109	[DO SAT = 7.7 mg/L]	Surface
Bontfield FAS (frm L. bank)	6 m	40 cm	26.2	8.4	112	[DO SAT = 7.5 mg/L]	Bottom
(2262 ft)	6 m	0 cm	26.2	8.1	108	[DO SAT = 7.5 mg/L]	Surface
8/15/2006, 2:30 PM	30 m	35 cm	24.5	8.2	108	[DO SAT = 7.6 mg/L]	Bottom
	30 m	0 cm	24.5	8.0	105	[DO SAT = 7.6 mg/L]	Surface
	60 m	70 cm	24.2	8.4	109	[DO SAT = 7.7 mg/L]	Bottom
	60 m	0 cm	24.2	8.5	110	[DO SAT = 7.7 mg/L]	Surface
	80 m	80 cm	24.1	8.5	110	[DO SAT = 7.7 mg/L]	Bottom
	80 m	0 cm	24.1	8.5	110	[DO SAT = 7.7 mg/L]	Surface
	95 m	1.0 m	24.1	8.3	108	[DO SAT = 7.7 mg/L]	Bottom
	95 m	0 cm	24.2	8.5	110	[DO SAT = 7.7 mg/L]	Surface
Bontfield FAS (frm R bank, in boat)	25 m	0.5 m	24.7	8.5	112	[DO SAT = 7.6 mg/L]	Surface
	25 m	1.0 m	24.7	8.5	112	[DO SAT = 7.6 mg/L]	Middle
	25m	1.5 m	24.75	8.5	112	[DO SAT = 7.6 mg/L]	Bottom
Roche Jaune FAS (frm R bank)	15 m	25 cm	22	7.4	93	[DO SAT = 8.0 mg/L]	Bottom
(~2300 ft)	27 m	29 cm	22.1	4.5	56	[DO SAT = 8.0 mg/L]	Bottom, in <i>Cladophora</i> beds
8/17/2006, 12:05 PM	27 m	0 cm	22.1	7.7	96	[DO SAT = 8.0 mg/L]	Above <i>Cladophora</i> beds
	37 m	32 cm	22.2	4.6	58	[DO SAT = 8.0 mg/L]	Bottom, in <i>Cladophora</i> beds
	37 m	0 cm	22.2	7.3	91	[DO SAT = 8.0 mg/L]	Above <i>Cladophora</i> beds
	50 m	34 cm	22.2	6.4	80	[DO SAT = 8.0 mg/L]	Bottom, in <i>Cladophora</i> beds
	50 m	0 cm	22.1	7.5	94	[DO SAT = 8.0 mg/L]	Above <i>Cladophora</i> beds
	80 m	39 cm	22.2	7.4	93	[DO SAT = 8.0 mg/L]	Bottom algal mats thin here
	80 m	0 cm	22.2	7.6	95	[DO SAT = 8.0 mg/L]	Surface
	100 m	58 cm	22.1	7.3	91	[DO SAT = 8.0 mg/L]	Bottom
	100 m	0 cm	22.2	7.6	95	[DO SAT = 8.0 mg/L]	Surface
	110 m	75 cm	22.2	7.6	95	[DO SAT = 8.0 mg/L]	Bottom
	110 m	0 cm	22.2	7.6	95	[DO SAT = 8.0 mg/L]	Surface
Fallon Bridge FAS (from L. bank)	10 m	39 cm	21.5	7.6	95	[DO SAT = 8.0 mg/L]	Bottom
2204 ft	10 m	0 cm	21.5	7.4	93	[DO SAT = 8.0 mg/L]	Surface
8/17/2006	25 m	63 cm	21.6	7.3	91	[DO SAT = 8.0 mg/L]	Bottom
	25 m	0 cm	21.7	7.4	93	[DO SAT = 8.0 mg/L]	Surface
	35 m	80 cm	21.7	7.2	90	[DO SAT = 8.0 mg/L]	Bottom
	35 m	0 cm	21.7	7.4	93	[DO SAT = 8.0 mg/L]	Surface
	50 m	51 cm	21.7	7.2	90	[DO SAT = 8.0 mg/L]	Bottom
	50 m	0 cm	21.7	7.6	95	[DO SAT = 8.0 mg/L]	Surface
	60 m	1.0 m	21.7	7.5	94	[DO SAT = 8.0 mg/L]	Bottom
	60 m	0 m	21.7	7.7	96	[DO SAT = 8.0 mg/L]	Surface
Intake FAS (from R bank, in boat)	85 m	50 cm	20.1	8.0	94	[DO SAT = 8.5 mg/L]	Just off the bottom
2072 ft	128 m	0 cm	20.1	8.1	101	[DO SAT = 8.5 mg/L]	Midchannel; 90 cm max depth
8/18/2006; wetted width = 234 m	128 m	80 cm	20.1	8.1	101	[DO SAT = 8.5 mg/L]	Midchannel; 90 cm max depth
Site Name, Elevation (ft)	Distance From Shore	Site Depth	Temperature (°C)	DO (mg/L)	DO (% SAT)	Saturation	Notes
Elk Island WMA (frm L. bank)	20 m	45 cm	20.8	7.3	88	[DO SAT = 8.3 mg/L]	Bottom
1939 ft	20 m	0 cm	20.7	7.8	94	[DO SAT = 8.3 mg/L]	Surface
8/18/2006, 1:50 pm	30 m	70 cm	20.6	7.7	93	[DO SAT = 8.3 mg/L]	Bottom
	30 m	0 cm	20.6	7.6	92	[DO SAT = 8.3 mg/L]	Surface
	40 m	80 cm	20.6	7.7	93	[DO SAT = 8.3 mg/L]	Bottom
	40 m	0 cm	20.6	7.7	93	[DO SAT = 8.3 mg/L]	Surface
	50 m	95 cm	20.6	7.7	93	[DO SAT = 8.3 mg/L]	Bottom
	50 m	0 cm	20.6	7.8	94	[DO SAT = 8.3 mg/L]	Surface
	60 m	1.05 m	20.6	7.9	95	[DO SAT = 8.3 mg/L]	Bottom
	60 m	0 m	20.7	7.9	95	[DO SAT = 8.3 mg/L]	Surface
Seven Sisters WMA (from L. bank)	10 m	1.0 m	20.5	8.0	96	[DO SAT = 8.3 mg/L]	Bottom
~1900 ft	10 m	0 m	20.4	8.0	96	[DO SAT = 8.3 mg/L]	Surface
8/18/2006							
Richland Park (frm L. bank)	1.0 m	1.5 m	21.2	7.3	88	[DO SAT = 8.3 mg/L]	Bottom
1900 ft	1.0 m	0 m	21.2	7.8	94	[DO SAT = 8.3 mg/L]	Surface
8/18/2006, 6:00 pm							

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Site Name, Elevation (ft)	Distance From Shore	Site Depth (ft)	Velocity (m sec ⁻¹)	Notes
Far West FAS (frm L bank)	~1 m	1.8	0.15	Approx. dist. From shore
(2480 ft)	~3 m	2.35	0.23	Near bottom
8/14/2006, 6:35 PM	~6 m	2.55	0.3	Near bottom
	~9 m	2.75	0.1	Near bottom
	~12m	3	0.22	Near bottom
	~15 m	3.01	0.33	Near bottom
	~17 m	3.25	0.31	Near bottom
	~17 m	3.25	0.24	Near bottom
Kinsey Bridge FAS (frm L bank)	10 m	1.1	0.1	Near bottom
(2326 ft)	15 m	1.4	0.18	Near bottom
8/15/2006, 12:10 PM	20 m	1.7	0.18	Near bottom
	25 m	1.7	0.21	Near bottom
	30 m	1.51	0.23	Near bottom
	35 m	1.45	0.15	Near bottom
	40 m	1.35	0.11	Near bottom
	45 m	1.05	0.15	Near bottom
	50 m	0.8	0.26	Near bottom
	55 m	1.7	0.22	Near bottom
	60 m	2.2	0.06	Near bottom
	65 m	2.35	0.06	Near bottom
	70 m	1.3	0.12	Near bottom
	75 m	1.45	0.21	Near bottom
	80 m	2.5	0.28	Near bottom
	85 m	2.45	0.29	Near bottom
Bonfield FAS (frm L bank)	15 m	1	0.08	Near bottom
(2262 ft)	30 m	1	0.07	Near bottom
8/15/2006, 2:30 PM	45 m	1.35	0.11	Near bottom
	60 m	1.65	0.19	Near bottom
	70 m	1.9	0.15	Near bottom
	80 m	2.3	0.19	Near bottom
	90 m	2.6	0.11	Near bottom
	100 m	2.6	0.18	Near bottom
	110 m	2.35	0.38	Near bottom
	115 m	3	0.13	Near bottom
Roche Jaune FAS (frm R bank)	15 m	0.4	0.13	Near bottom
(~2300 ft)	25 m	0.35	0.08	Near bottom
8/17/2006, 12:05 PM	35 m	0.35	0	In Cladophora bed
	35 m	0	0.07	Above Cladophora bed
	45 m	0.6	0.001	In Cladophora bed
	45 m	0	0.07	Above Cladophora bed
	55 m	0.45	0.02	In Cladophora bed
	55 m	0	0.15	Above Cladophora bed
	65 m	0.45	0.07	Near bottom
	75 m	0.45	0.17	Near bottom
	85 m	0.5	0.24	Near bottom
	95 m	0.6	0.34	Near bottom
	105 m	1.05	0.24	Near bottom
	115 m	1.9	0.36	Near bottom
	125 m	2.45	0.34	Near bottom
Site Name, Elevation (ft)	Distance From Shore	Site Depth (ft)	Velocity (m sec ⁻¹)	Notes
Fallon Bridge FAS (from L bank)	15 m	1.1	0.11	Near bottom
2204 ft	20 m	1.4	0.14	Near bottom
8/17/2006	25 m	1.5	0.14	Near bottom
	30 m	1.95	0.15	Near bottom
	35 m	2.25	0.1	Near bottom
	40 m	2.2	0.03	Near bottom
	45 m	2	0.11	Near bottom
	50 m	1.7	0.12	Near bottom
	55 m	1.55	0.14	Near bottom
	60 m	1.05	0.09	Near bottom
	65 m	1	0.09	Near bottom
	70 m	1.9	0.19	Near bottom
	75 m	3.2	0.18	Near bottom
Intake FAS (from R bank, in boat)	85 m	0	0.54	Surface
2072 ft	85 m	2	0.26	Near bottom
8/18/2006, wetted width = 234 m	128 m	0	0.36	Surface
	128 m	2.6	0.19	Near bottom
Elk Island WMA (frm L bank)	10 m	0	0.14	Surface
1939 ft	10 m	0.85	0.35	Bottom
8/18/2006, 1:50 pm.	20 m	0	0.18	Surface
	20 m	1.6	0.16	Bottom
	30 m	0	0.22	Surface
	30 m	2.05	0.14	Bottom
	40 m	0	0.2	Surface
	40 m	2.55	0.11	Bottom
	50 m	0	0.24	Surface
	50 m	2.6	0.12	Bottom
	55 m	0	0.22	Surface
	55 m	2.9	0.14	Bottom
	60 m	0	0.22	Surface
	60 m	3.15	0.17	Bottom
	65 m	0	0.24	Surface
	65 m	3.15	0.15	Bottom
Seven Sisters WMA (from L bank)	10 m	0	0.17	Surface
~1900 ft	10 m	2.25	0.06	Bottom
8/18/2006	15 m	0	0.28	Surface
	15 m	3.65	0.08	Bottom
Richland Park (frm L bank)	0.6 m	0	0.93	Surface
1900 ft	0.6 m	3	0.18	Bottom
8/18/2006, 6:00 pm				

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the
Yellowstone River

USING A COMPUTER WATER-QUALITY MODEL TO DERIVE NUMERIC NUTRIENT CRITERIA FOR A SEGMENT OF THE YELLOWSTONE RIVER

Quality Assurance Project Plan-Addendum

Prepared for:

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November 6, 2007

Purpose of this Addendum

During the sampling phase of the Yellowstone River project (July 30 -September 23, 2007), several modifications to the original QAPP were necessary due to realities encountered in the field. This addendum documents these changes. Each section number below refers to the corresponding section in the original QAPP. It is recommended that the reader review the original QAPP prior to reading this document. Explanations as to why the change was needed are provided with each.

Section 3.1 Primary Question, Objectives and River Reach Description

Modifications to the site locations, and rationales for the changes, are shown in Table 3.1. A further explanation is necessary for the Kinsey Bridge FAS modification (Table 3.1). It was intended that the new site (Yellowstone River @ river mile 375) would completely replace the Kinsey Bridge FAS site. However, dropping water levels during the August sampling event created river hazards for the boat, and therefore the YSI was moved downstream to the Kinsey Bridge FAS (which could be accessed by road). Thus, the dataset for the Yellowstone River zone downstream of the Tongue River & Miles City WWTP is in two parts; data collected at river mile 375 (through August 22nd), and data collected at the Kinsey Bridge FAS (August 22nd-September 19th).

Table 3.1 Addendum. Modification of site locations.

Originally Proposed Site	Modification	Explanation
Yellowstone River @ Kinsey Bridge FAS	Yellowstone River @ river mile 375, 5.5 miles upstream of Kinsey Bridge	The original intent of the Kinsey Bridge site was to detect potential influences from the Tongue River and Miles City WWTP. The modified site (river mile 375) was deemed better because it was closer to these river influences (new site was 4 miles downstream of WWTP, Kinsey Bridge was 9.5 miles downstream).
Yellowstone River upstream of Powder River & Shirley Main Canal confluences	Yellowstone River just upstream of Powder River confluence	Dirt road access to site upstream of Powder River had potential (during rain) to render the site impassable for boat & trailer. Boat was required to get upstream of Shirley Main Canal confluence. YSI could be retrieved from modified site without the boat, if required.
Yellowstone River 11 miles upstream of Glendive	Yellowstone River @ Fallon Bridge FAS	Reaching the Yellowstone River 11 miles upstream of Glendive required either boat travel from Glendive or a local launch site. No local launch was found, and boat travel from Glendive was deemed too hazardous due to rocks and the river's shallowness.

Section 3.2.3 Sediment Oxygen Demand Measurements Using Benthic Chambers

Modifications to SOD Measurement. Measurement of SOD in a river system proved to be very different than what I have experienced in lentic systems. The YSI 6600 sonde dissolved oxygen (DO) data from the first set of duplicated SOD incubations (reviewed in the field) revealed that DO, instead of decreasing over time (as expected), increased instead. As DO increased throughout the day in the river, so too did DO in the chambers. Because the chambers have a skirt that penetrated into the river bottom 10 cm, I believe the DO increase was due to a proportion of river water moving through the coarse gravels of the river bed below the chambers' skirt which then mixed (to some unknown degree) with the water in the chambers. To help control for this, subsequent SOD measurements were carried out with one YSI 6600 sonde in the benthic chamber (experiment) and the other YSI 6600 sonde attached to the outside of the chamber in the flowing river water (control). This arrangement precluded duplicate chamber incubations because we only had the two YSI sondes available.

Other Sediment Fluxes Not Measured. Due to time constraints and the influence of dilution from through-gravel flows into the benthic chambers, we deemed it impractical to measure sediment fluxes of DIC, SRP and ammonia.

Section 4.1 Quality Criteria for Benthic Chamber SOD

Because of the issues described above, we only carried out duplicate SOD chambers once. This single duplicated event will have to suffice for comparison with the *a priori* quality criteria proposed for SOD measurements (CV of $\pm 20\%$ among duplicates).

Section 4.2 Quality Criteria for YSI 6600 EDS Sondes Deployed Long-Term

Biofouling from Drifting Algae. The QAPP addressed means by which biofouling would be managed (periodic cleaning, use of YSI sondes with automatic wiper functions on the probes). However, the type of biofouling anticipated was growth and colonization on the deployer & sondes, and it resulted that this type of growth was fairly light in the Yellowstone River and the wiper mechanisms were clearly capable of keeping the probe faces clean. The major potential biofouling interference came from drifting filamentous algae. Although the deployers were designed to hydro-dynamically shunt drifting algae around the sondes, in some cases drifting algae was so heavy that a build up of snared algae filaments began to smother the probe-end of the YSI sondes. Notes and photographs were taken during each visit as to the overall status of the deployer/sonde units (e.g.,—snared drifting algae light, no problems anticipated||; or—heavy algae accumulation, readings may be interfered with||). These notes will be used to help assess data quality (see below).

YSI data were cross-checked in September using a second, calibrated YSI placed near the deployed YSI at the time it was to take a reading (every quarter hour). These cross-checks were made prior to the time the deployed YSI was cleaned. These data will be used to help identify cases where snared drifting algae or other problems were causing instrument interference.

A posteriori Protocols for Screening YSI Sonde Data. Criteria were developed in Section 4.2 of the QAPP to address anticipated factors that could affect the YSI sonde's data quality (instrument drift, biofouling). However, we did not outline a process for segregating data we have high confidence in from data that may be compromised by biofouling or other problems. Therefore, an *a posteriori* process is here defined, and will be applied to each YSI sonde dataset so that high quality data is retained and used in model development.

- A. Data logged while a deployed instrument was out of the water for cleaning will be flagged—R|| (data rejected, per Modern STORET).
- B. When data drift is outside of the criteria established in the QAPP (criteria were established for DO, turbidity, and Chl *a*), we will flag the data back to the previous known point of calibration with—BD|| (Beyond allowable Drift).
- C. Data from a deployed YSI sonde will be compared to data from the cross-check YSI sonde. In cases where the cross-check sonde data differ substantially from the deployed-sonde data, the deployed data will be flagged with the letters—DX|| (Differs from Cross-Check). Allowable variation between the cross-check and deployed instruments are as follows:
 - a. Dissolved Oxygen: 0.5 mg/L (instrument accuracy = 0.2 mg/L, X 2 instruments, plus 0.1 mg DO/L for spatial variation¹)
 - b. pH: 0.5 standard units (instrument accuracy = 0.2, X 2 instruments, plus 0.1 unit for spatial variation¹)
 - c. Temperature: 0.4°C (instrument accuracy = 0.15°C, X 2 instruments, plus 0.1°C for spatial variation¹)
- D. When field notes indicate that a YSI sonde may have been overwhelmed by snared drifting algae, we will:
 - a. Review the dataset immediately before and after the cleaning of the unit. Where there is a sharp shift in measured values following a cleaning, the dataset following the cleaning will be considered the preferable one for modeling purposes.
 - i. When sharp change in data values occurs after a cleaning event, an attempt will be made to determine when the interference began. The dataset will be reviewed from the last point of known status (i.e., initial deployment or previous cleaning) up to the cleaning event where the sharp change was noted. Data review will focus on data types that manifest diel patterns (pH, DO). These will be reviewed for (1) sudden, unexplainable

¹ YSI cross-checks were taken prior to identifying the exact location of the deployed YSI, in order to prevent any disturbance to the deployed unit. As such, the cross-check unit was usually only within 1-5 meters of the location of the deployed unit due to limited water clarity. This spatial difference is another source of difference between deployed vs. cross-check measurements. Therefore, it is accounted for (as best possible) with this additional allowable variation factor.

change in the magnitude of the daily patterns inconsistent with the pattern immediately proceeding the change, and (2) large, unexplainable scatter of individual data points inconsistent with the overall diel patterns. Data that meet the conditions in (1) and (2) that have no reasonable explanation (e.g., there was a corresponding spike in turbidity that dampened diel DO variation) will be flagged with—I I| (Instrument Interference).

USING A COMPUTER WATER-QUALITY MODEL TO DERIVE NUMERIC NUTRIENT CRITERIA FOR A SEGMENT OF THE YELLOWSTONE RIVER

Sampling and Analysis Plan

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APPENDICES

- Appendix A: *Internal DEQ memo supporting dye tracer study on Yellowstone River*
- Appendix B: *Project Equipment Checklist*
- Appendix C: *Inventory of Project Activities, Listed by Site*
- Appendix D1: *Benthica and Algae Cross-section Measurement Field Form*
- Appendix D2: *Sediment Oxygen Demand and Solute Flux Field Form*
- Appendix D3: *Phytoplankton Productivity Field Form*

1.0 Introduction and Background Information

The intent of this sampling and analysis plan (SAP) is to support the project detailed in the quality assurance project plan (QAPP) of the same name. Please refer to Section 2.0 —Introduction of the QAPP for details on the background and rationale for the project.

2.0 Objectives and Design of the Investigation

2.1 Primary Question and Objectives

The project outlined in this SAP is designed to answer the following question:

In a segment of the lower Yellowstone River, what are the highest allowable concentrations of nitrogen and phosphorus which will not cause benthic algae to reach nuisance levels and/or dissolved oxygen concentrations to fall below applicable State water quality standards?

Sampling described herein is intended to support the QAPP, and is intended be completed in 2007. The only exception to this is the dye-tracer study, which will probably be undertaken in summer 2008. If the dye-tracer study is completed in 2008, the results from it will be used to further refine the model, which should be developed by that time.

2.2 Overview of What Will be Measured, Where, and How Often

Table 2.1 provides the description, frequency and location of measurements planned for summer 2007. The plan was developed following recommendations outlined in an EPA manual (Mills et al., 1986). EPA's manual provides guidance on designing monitoring plans intended to work in conjunction with the QUAL2E model. Fig. 2.1 shows the targeted reach of the Yellowstone River, and the types of measurements that will be made at various locations throughout. **This information is also provided Appendix C, listed as activities per site, which should be used during field work to track what has been completed.**

USING A COMPUTER WATER-QUALITY MODEL TO DERIVE NUMERIC NUTRIENT CRITERIA FOR A SEGMENT OF THE YELLOWSTONE RIVER

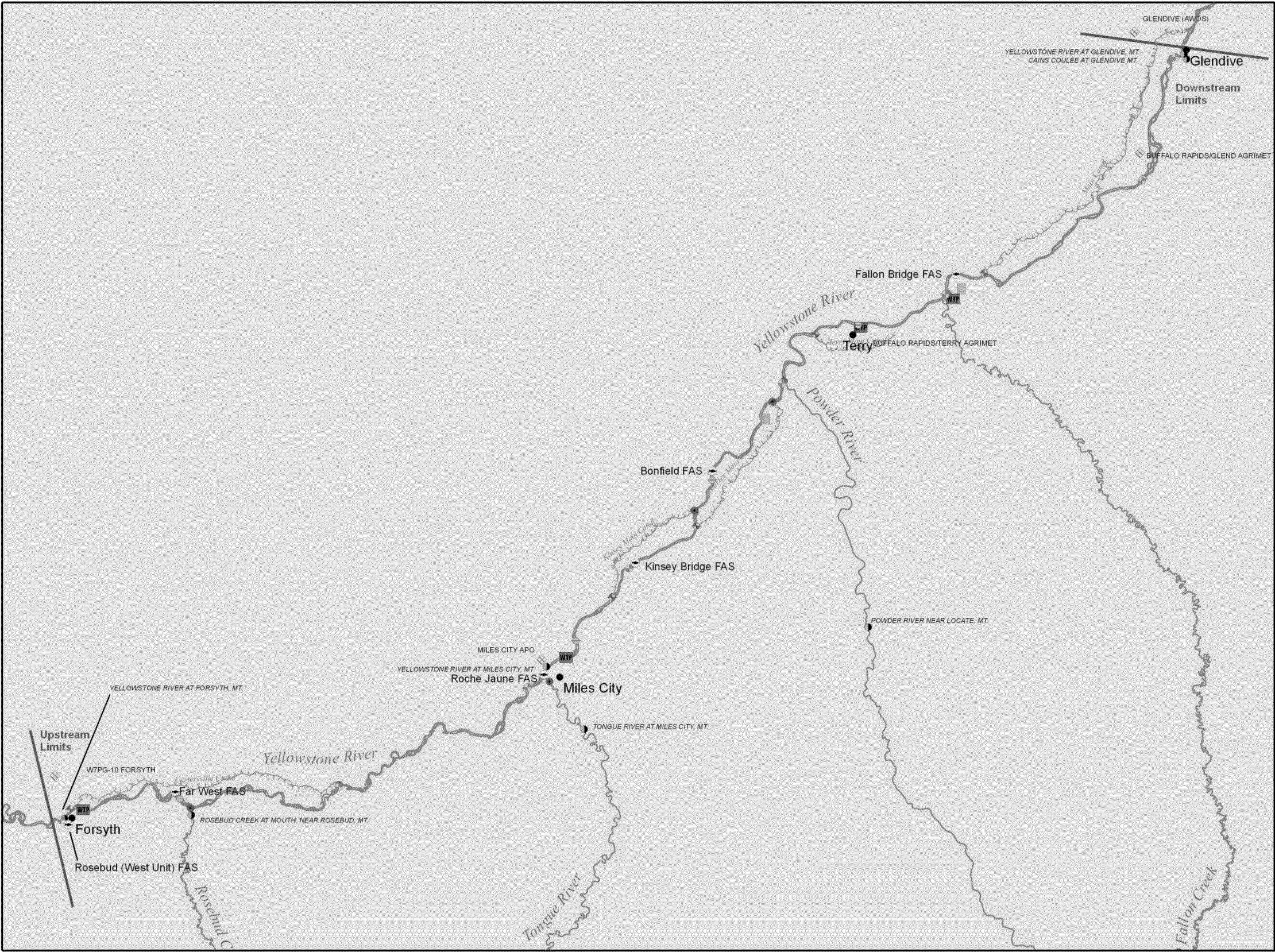
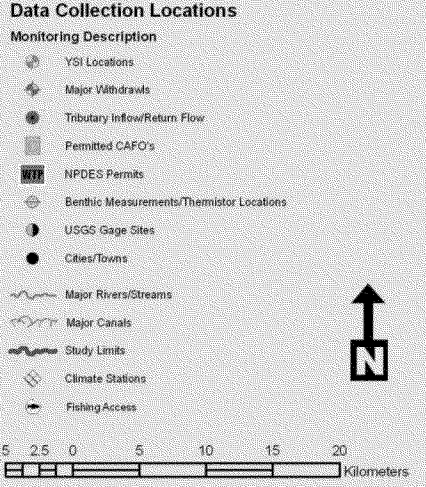


Figure 2.1. Yellowstone River QUAL2K Monitoring Locations



Yellowstone River Project Vicinity



Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Table 2.1 Frequency, Location and Description of Measurements for the Project, Summer 2007.

Measurement (& QUAL2K symbol, if applicable)	Units	How Often Measured	Where Measured
<u>Benthic Chamber Measurements</u>			
Sediment Oxygen Demand (SOD)	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
Water O ₂ Demand to Correct SODs (WOD)	$\text{mg O}_2 \text{ m}^{-3} \text{ hr}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
Ammonia flux (J_N)	$\text{g N m}^{-2} \text{ day}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
Methane flux (J_{CH_4}) <i>Collection and analysis optional</i>	$\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
DIC flux (J_C) — for RQ calculation	$\text{g C m}^{-2} \text{ day}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
<u>Other Rate Measurements</u>			
Photosynthesis of phytoplankton, via light/dark bottles ($k_{\text{app}}(\Gamma)$)	$\text{mg C m}^{-3} \text{ hr}^{-1}$	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
Photosynthesis of bottom-attached <i>Cladophora</i>	$\text{mg C m}^{-3} \text{ hr}^{-1}$	Twice (Aug-Sept)	Roche Jaune FAS.
<u>Benthic Measurements</u>			
Benthic algae Chl <i>a</i> , and AFDW	mg m^{-2}	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
% bottom covered by heavy benthic algae at each transect	%	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
% river bottom to which SOD values apply	%	Twice (Aug-Sept)	Far West FAS, u/s of Tongue R. (Ft. Keogh Bridge), Pirogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Creek confluence, 11 miles u/s of Glendive.
<u>Real Time Water Quality Measurements (YSI 6600EDS)</u>			
Dissolved Oxygen (o)	$\text{mg O}_2/\text{L}$	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.
pH	Standard	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.
Temperature	° C	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.
Specific Conductivity	$\mu\text{S}/\text{cm}$	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.
Chl <i>a</i> (fluorometric, calibrated to real samples)	$\mu\text{g Chl } a / \text{L}$	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.
Turbidity	NTU	24/7, early Aug to Sept 30	Rosebud (West Unit) FAS, u/s of Carterville Canal return, u/s of Tongue R. (Ft. Keogh Bridge), Kinsey Bridge FAS, u/s of Powder R./Shirley Main confluence, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive, old Bell St. Bridge in Glendive.

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Table 2.1, Cont. Frequency, Location and Description of Measurements for the Project, Summer 2007.

Measurement (& QUALOR symbol, if applicable)	Units	How Often Measured	Where Measured
Water Samples			
Total phosphorus (TP)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Total nitrogen (TN)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Nitrate + nitrite (NO ₃ -N)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Total ammonium (NH ₄ ⁺)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Dissolved organic nitrogen (DON)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Dissolved organic phosphorus (DOP)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Soluble reactive phosphate (SRP)	µg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Turbidity	NTU	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
SSC (suspended sediment concentration)	mg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Total Inorganic Carbon (C _T) Also referred to as Dissolved Inorganic Carbon (DIC)	mg/L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Phytoplankton Chl a (a _{ph})	µg Chl a /L	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Seston CN:P ratio	dimensionless	Twice (Aug-Sept)	Yellowstone: Buffalo Mirage FAS (Comparison), Rosebud (West Unit) FAS, w/s of Carterville Canal return, w/s of Tongue (Ft. Keogh Bridge), Kinsey Bridge FAS, w/s of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Cr. confluence, 11 miles w/s of Glendive, old Bell St. Bridge in Glendive. Tribes/other: Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River at mouth, Terry Main Canal return point.
Other Measurements			
PERL-1 diatom population samples		Twice (Aug-Sept)	Buffalo Mirage FAS, Far West FAS, w/s of Tongue (Ft. Keogh Bridge), Frogue Island State Park, Bonfield FAS, Terry Bridge, upstream of O'Fallon Cr. confluence, 11 miles upstream of Glendive.
Meteorological (wind speed, temp, humidity)	various	Early Aug to Sept 30	Island in Yellowstone R. within the Fort Keogh Ag. Experiment Station.
Water Temperature (Collected hourly via Hobo dataloggers)	° C	Early Aug to Sept 30	Buffalo Mirage FAS, Far West FAS, Frogue Island State Park, Bonfield FAS, Terry Bridge.
River Width	m	Twice (Aug-Sept)	All sites.
River mean Depth	m	Twice (Aug-Sept)	All sites, except specified benthic sites (See Appendix C).
River velocity	m sec ⁻¹	Twice (Aug-Sept)	All other benthic chamber sites.
Flow (DEQ measured)	m ³ sec ⁻¹	Twice (Aug-Sept)	Yellowstone River: Upstream of Carterville Canal return, upstream of Powder River/Shirley Main Canal confluence, upstream of O'Fallon Creek confluence, 11 miles w/s of Glendive. Tribes/other: Carterville Canal at withdrawal, Carterville Canal return point, Tongue River nr mouth, Kinsey Main Canal withdrawal, Shirley Main Canal withdrawal, Kinsey Main Canal return point, Shirley Main Canal return point, Powder River nr mouth, Terry Main Canal withdrawal, O'Fallon Cr. near confluence.
USGS Discharge	m ³ sec ⁻¹	annually - USGS	Yellowstone River at Forgyth, Tongue River at Miles City, Yellowstone River at Miles City, Yellowstone River at Glendive.

3.0 Field Sampling Methods

3.1 Sediment Oxygen Demand, Benthic Chambers, & Solute Fluxes

In Situ Measurement of SOD Using Benthic Chambers, Summer 2007. The chambers will be deployed in pairs at each of the sites indicated in Fig 2.1, Table 2.1 and Appendix C, and will use the YSI 6600EDS sonde and the YSI 85 probe to measure changes in DO and temperature within the chamber.

Chambers will be pressed in to the sediments and then anchored to the bottom using a heavy iron chain wrapped several times around the flexible skirt, so that a good seal between the river bottom and chamber is assured. The chambers will be located on relatively flat sediments in near-shore areas up to 1 meter deep, which can be reached by wading from shore. Based on the near-bottom water velocity measured at the chamber site (using a Marsh-McBirney flow meter, in m sec^{-1}), either the low-flow or high-flow pumps will be selected for attachment to each chamber. After chamber emplacement, within-chamber water will be exchanged with external river water for 2 minutes. The pump will be set on a low-flow setting and its inflow will be disconnected from the chamber so that clean river water can be drawn in and flushed through the chamber. The chamber outflow port will be opened during this time to assure exchange with the external river water. After purging the chamber for 2 minutes, the hose will be reattached and the chamber re-sealed, and the within-chamber water velocity will be adjusted (via the flow-control valve on the pump) to simulate the velocity measured near the river bottom at the site. Periodic checks using the hand-held YSI 85 will be undertaken to monitor chamber DO decline; the incubation will be terminated when a notable decline in DO has occurred.

Changes in the DO of the water within chambers (WOD) will be determined in six 300 ml BOD dark bottles (3 initial, 3 final). The 3 initial bottles will be filled with river water and fixed (Lind 1979) at the time the chambers are emplaced, while the 3 final bottles will be filled and then incubated at ambient river temperatures for the duration of the SOD incubation, then fixed. All 6 will be measured for DO via the Winkler titration method, completing the titration step within 3 days of collection.

The SOD ($\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$) will be calculated, per Droic and Koncan (1999), as:

$$\text{SOD} = \frac{aV - bV}{S} \quad (1)$$

Where a is the slope of the time-DO curve for a chamber with combined sediment & water DO-demand ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$), b is the mean slope of the 3 time-DO curves for water in the dark BOD bottles ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$), V is the volume of overlaying water in a chamber interfaced with the sediments (m^3), and S is the area of sediment covered by a chamber (m^2).

Solute Fluxes to be Measured Using the In Situ Benthic Chambers. Ammonia, dissolved inorganic carbon (DIC) and methane fluxes are to be measured in the benthic chambers.

Measurement of methane is, at this writing, optional, as the laboratories identified for the project may not be able to carry out its measurement.

After the chambers have been emplaced, purged and then sealed, water samples for ammonia, methane (*optional*) and DIC will be collected from each chamber at a valve-operated access port using a 60 cc syringe with a luer-lock tip. A second inlet valve will be opened during sample collection to allow an equal volume of river water to enter the chamber and replace that withdrawn during sample extraction. After collection, both valves will be shut. A 2nd set of samples will be collected at the end of the incubation. Concentration change over time for each solute equals the solute's flux.

DIC samples will be carefully filtered using 0.45 µm filters and overflowed in to their sample bottle, without bubbles, until about two sample-bottle volumes have been purged, and then stored without headspace in the bottle on regular ice. **Ammonia** samples will be 0.45 µm filtered, filled to minimize bottle head space, and then frozen on dry ice.

3.2 Other Rate Measurements

Phytoplankton Growth Rates. QUAL2K allows the user to input maximum photosynthesis rates at a given temperature (kgp[T]; Chapra and Pelletier, 2003). Phytoplankton growth rates will be measured using the light-dark bottle technique (Lind, 1979; EPA, 1983; Wetzel and Likens, 1991).

Depth/width integrated water samples (see Section 3.5 on collection of a depth/width integrated water sample) will be used to fill triplicate dark bottles and light bottles. Both light and dark bottles will be incubated *in situ*, under ambient light conditions at or near the water's surface, using the BOD bottle racks, as close to midday as possible. This will provide maximum field-measured photosynthesis rate (EPA, 1983). Incubations will normally be completed within 2-4 hours, at which time the incubation will be terminated by chemical fixation and subsequent DO measured via the Winkler titration method (Wetzel and Likens, 1991; APHA, 1998). **If the titration step of the procedure cannot be completed immediately, place the flocculated & acidified (fixed) samples on ice in the dark for up to a maximum of 3 days.** SEE INSTRUCTIONS ON PAGES 72-77 OF Lind (1979). Samples held in this manner will be warmed to room temperature in the dark prior to completion of the sodium thiosulfate titration step.

Cladophora Influence on DO. Where dense *Cladophora spp.* beds are present, for example the Roche Jaune FAS, DO uptake of *Cladophora* samples will be measured in duplicate 300 ml dark bottles using a YSI model 85 meter. The intent of this measurement is to determine the proportion of DO consumption from the algae relative to the water and sediments, in locations where this alga is obviously a significant nighttime DO sink. DO demand values derived from these measurements can be used to help cross-check outputs from QUAL2K. The calculated rate will be adjusted for the DO change associated with the phytoplankton as measured in the light/dark bottles above.

Blobs of *Cladophora* algae of known mass (squeezed wet weight) will be placed in duplicate dark bottles and the change in DO over time will be measured using a calibrated YSI model 85 meter. The volume occupied by the algae will not exceed about 50% of the bottle. The meter probe will be sealed at the bottle mouth with no air bubbles. Incubations will last 1-2 hrs, or until a 1 mg/L or greater DO drop has been measured. The bottles will be inverted several times prior to taking each DO measurement. Also, the area of river bottom covered by the algal beds will be estimated for a 50 m reach by eye, and the mass of *Cladophora* (squeezed wet weight) m^{-2} in the beds will be measured in 3 locations at the site using the hoop method.

3.3 Other Benthic Measurements

Benthic Algal Chl a , AFDW and Macrophyte DW. Field sampling methods will generally follow, with some exceptions and additions, the DEQ protocols outlined in the draft DEQ Standard Operation Procedure (SOP) manual,—Sample Collection and Laboratory Analysis of Chlorophyll- a , available at: <http://www.deq.state.mt.us/wqinfo/monitoring/SOP/sop.asp>. Results of the benthic algae sampling will be expressed as chlorophyll a (Chl a) and AFDW, and the macrophyte biomass as dry weight, in area units (mg m^{-2}).

The longitudinal reach layout described in the DEQ SOP cited above would create unduly long sampling reaches on the Yellowstone River. Instead, we will collect 11 individual samples at equidistant points across transects perpendicular to river flow, at specified sites indicated in Table 2.1 and Appendix C. The hoop, sediment core and template methods will be collected, as appropriate, at equidistant points along each transect.

Algae and macrophytes in hoop samples will be physically separated in the field, and each plant types' Chl a and mass will be measured separately in the laboratory. Some transect points will be beyond the reach of a wading person, and instead a boat will be used to collect benthic samples using a Ponar dredge. The boat will be anchored at the sampling point and bottom materials brought up by the Ponar dredge will be subsampled using either the template or sediment core method, as appropriate (the hoop method would not be workable in this situation, and will probably not be applicable in higher velocity areas of the river anyway). *Use Table 1 of Appendix D1 to record all relevant information for each transect point.*

For diatom community samples, a qualitative composite sample of representative benthic material (PERI-1) from each of the 11 transect collection points will be placed in a single 50 cc centrifuge tube, to a volume of 45 ml, and then preserved with formalin (5 ml). Wrap the cap of the tube with Parafilm wax.

Estimate of Algal Growth Cover and Proportion of Applicable Channel SOD. The % river bottom covered by visible algae growth and the % river bottom to which SOD measurements apply will be estimated at the sites specified in Table 2.1 and Appendix C. **During the transect collection of benthic algae**, a record will be made at each of the 11 sampling locales indicating the degree of algae coverage, the substrate class, and the near-bottom water velocity (Table 1, Appendix D1). Based on the information recorded in Table 1, Appendix D1, a final estimate of the % river bottom to which the SOD values apply will be made and recorded in Table 4, Appendix D2.

3.4 Real-Time Water Quality Measurements (YSI 6600EDS)

Data Collected Using the YSI 6600EDS Sondes. Water temperature, pH, DO, specific conductivity, turbidity and Chl *a* concentrations (Table 2.1) will be monitored, for up to six weeks across the study period, using YSI model 6600EDS sondes deployed in the river². The sondes have built-in dataloggers that can be programmed to collect data at pre-defined intervals, and will be set up to take water quality measurements every 30 min or 1 hr. They have a memory capable of storing up to 90 days of logged data, although a YSI representative indicated that 60 days in a more prudent timeframe. YSI's website states that the 6600 sondes have a 75 day battery life at 15 min logging intervals. The sondes will be calibrated in the laboratory according to the manufacturer's instructions (YSI, 2006), and checked again in the field prior to deployment.

Turbidity will be calibrated using the two-point method using 0, 11.2 and 100 NTU standards. **Conductivity** will be calibrated using a 1000 $\mu\text{S}/\text{cm}$ standard. The **pH** will be calibrated using the two-point method using pH 7 and 10 standards. **Chl *a*** measurements recorded by the YSI 6600EDS sonde are made using a fluorometric probe, and are relative; that is, to determine the true river Chl *a* values, they must be regressed against laboratory-measured Chl *a* samples, collected separately from the river at the same location³. To check instrument drift, the Chl *a* probe will be calibrated in the lab against a 2% Rhodamine WT dye standard (YSI 2006). **DO** will be calibrated, just prior to deployment, in a controlled environment (e.g., hotel room), using the single-point, water-saturated air or air-saturated water method (YSI, 2006).

The sondes are equipped with wipers that periodically clean the sensor surface and these will be activated upon deployment. The sondes may be painted with anti-fouling paint to prevent growth of biofouling aquatic life (YSI, 2006). To minimize problems due to biofouling, the sondes will be checked and cleaned of growth 25-30 days (study midpoint) after the initial deployment. If recalibration is required, as determined from field checks against standard solutions, instrument drift (probe reading vs. standard) will first be recorded prior to re-calibration.

During the sampling runs in mid-August and mid-September, measurements of DO, temperature and specific conductivity will be taken from the boat using a calibrated hand-held YSI (model 85) as near to the deployed sondes as feasible, to cross-check the sondes' data (post deployment). Upon sonde retrieval at the *end* of the project, sonde readings will be compared to laboratory standards for pH, conductivity, etc. to determine instrument drift. DO drift will be checked by using the sonde to measure DO via the single-point, water-saturated air method.

² The YSI placed 11 miles upstream of Glendive is an older model, and because of this it can measure all parameters except turbidity. Also, its DO probe will be the earlier, polarographic type, which will be recalibrated after 25-30 days of the initial deployment.

³ At least 4 Chl *a* water samples will be collected at each long-term sonde deployment site during the study period in order to calibrate the probe measurements. Collection locations and frequency for Chl *a* are shown in Table 2.1; Chl *a* samples procedures for laboratory-analyzed Chl *a* samples are detailed in Section 3.5.

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Deployment System for YSI 6600EDS Sondes. During the reconnaissance trip (Aug 2006), we investigated means by which the YSI 6600EDS sondes could be mounted for extended periods in the river (up to 2 months), with some degree of security. The river could not be accessed from the bridge deck of any of the bridges we visited, therefore the sondes will have to be attached to the bridge support columns from the water, or by some other means.

The design shown in Fig. 3.1 was developed for this purpose. The river bottom at all sites in this reach of the Yellowstone River is fairly hard (gravel and sand), and the weighted block of the deployer should not sink in to the bottom any significant distance. The weighted block of the deployer will hold the assembly on the river bottom, and the sonde itself will be maintained in the river flow about 10-15 cm above the bottom. The device should be invisible from shore (except perhaps during very low flows) which should improve security. The brass ID plate embedded on the deployer will say—Water Quality Monitoring Equipment. Property of the State of Montana. If found, please call (406) 444-0831 or (406) 444-5964||. The deployer may be painted with anti-fouling paint to minimize algal and other growth accumulation.

The sonde deployer in Fig. 3.1 will be placed in the river using a boat. A 1/8 inch or smaller stainless steel cable will be looped around the bridge support, or a nearby tree, and then clamped in place with a swage. If no suitable attachment point can be located, an approx. 50 lb block with an eyebolt on it will be placed on the river bottom upstream of the deployer and the sonde deployer will be attached to it. The sonde deployer will then be placed 10-20 m downstream of the bridge support, tree or block, using the boat. The stainless steel cable will allow retrieval of the device as it can be snagged with a grappling hook from the boat. In cases where the device is attached to shoreline trees the cable will be buried, to the extent possible, upon deployment.

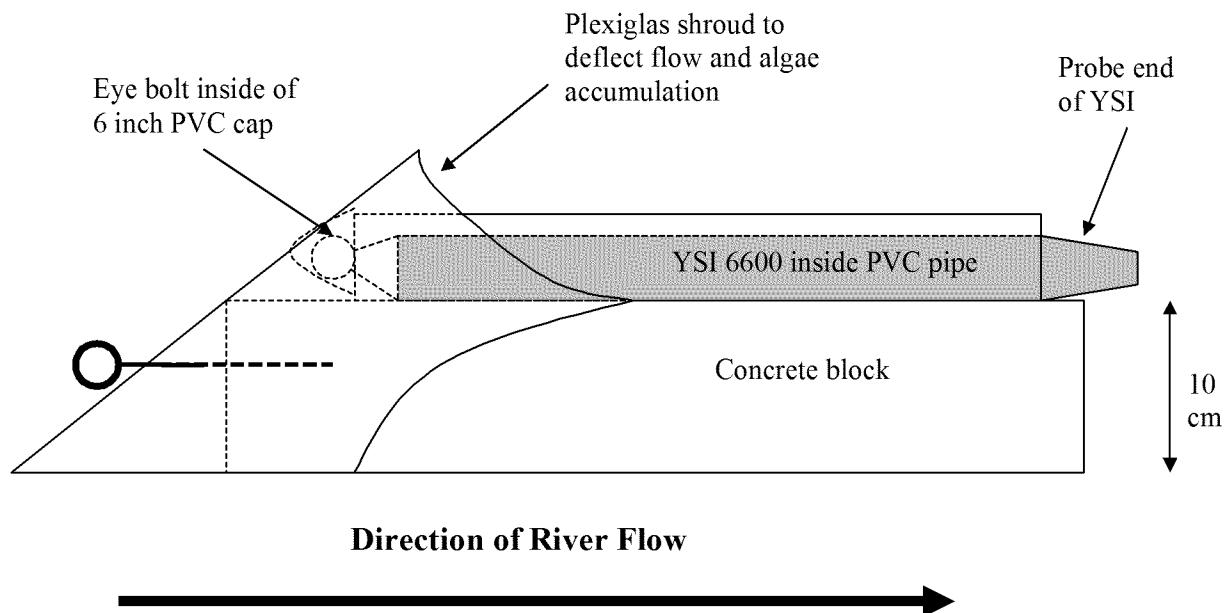


Fig. 3.1. Profile view of the YSI 6600EDS sonde deployment system.

3.5 Water Samples

The majority of nutrient and other water quality parameters shown under the—Water Samples component of Table 2.1 are routine, and QA/QC guidelines found in DEQ (2005) apply. Because of the width of the Yellowstone River, collecting representative water samples will require depth and width integration techniques rather than simple shore-line grab samples. (Canals will be grab-sampled only.)

A composite water quality sample will be collected concurrent with benthic algae sampling (see Section 3.3) as shown in Figure 3.2 using an equal-width-increment (EWI) sampling technique. At each of the 11 points along a transect, a vertically and horizontally integrated water sample (Wilde et al. 1999) will be collected using a DH48 (wading) or DH95 (boat-mounted) sampler. The 11 samples will be composited into a single carboy and subsamples will be withdrawn for each of water quality parameters of interest (Table 2.1). The plastic carboy will be gently churned (i.e. through light shaking) prior to collection of the samples. For total water-quality measurements (e.g., total P, total N, SSC), phytoplankton Chl *a* and seston, the water in the carboy will be thoroughly shaken and the sub-sample taken immediately.

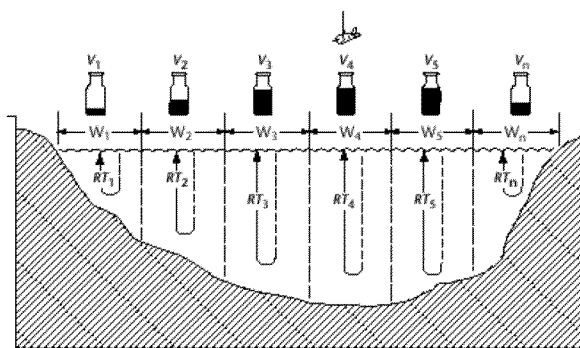


Figure 3.2. Equal Width Increment (EWI) Schematic.

Samples will be preserved and stored per DEQ SOPs (detailed in DEQ's field procedure manual at: G:\WQP\QA_Program\3_Standard Operating Procedures\2-Field Procedures Manual). A copy of the manual will be carried to the field for reference.

Water samples. All dissolved nutrient samples will be field-filtered ($0.45\ \mu\text{m}$). Both total nutrient and soluble nutrient samples will then be frozen immediately on dry ice without additional preservation. (If freezing is not possible, standard DEQ preservation methods with H_2SO_4 , etc. will be used. If this scenario arises, submit the preserved nutrient samples to the DPHHS laboratory *only*.) **Duplicates will be collected for 5% of all samples. Field/equipment blanks will be collected at the end of each sampling trip (one in August, one in September).** The DH samplers will be rinsed with 10% HCl and DI water between samplings. Detection limits, appropriate bottle sizes and preservative volumes for each parameter are found in Table 4.0 of DEQ (2005). Sample bottles are as follows:

1. Dissolved nutrients (NO_{2+3} , ammonia, DON, DOP, SRP). 250 ml bottle — $0.45\ \mu\text{m}$ filtered, then on dry ice
2. Total nutrients (TN, TP). 250 ml bottle — dry ice
3. Dissolved Inorganic Carbon. 250 ml bottle — on regular ice
4. Suspended sediment concentration (and Turbidity). 1 L bottle — on regular ice

QUAL2K prompts the user for the stoichiometry (C:N:P ratio) and mass of suspended organic matter (seston; living and detrital organic material). Seston will be measured for C, N and P content, dry weight and AFDW. The University of Montana Flathead Lake Biostation is capable of analyzing both CNP samples; the samples will be sent to them after completing the preliminary preparations outlined below. The 1st pair of filters will be analyzed for C & N content using the high temperature induction furnace method (American Society of Agronomy, 1996), and the 2nd pair for total P content using methods outlined in Mulholland and Rosemond (1992).

For CNP samples, dry weight and AFDW will be determined on GF/F filters used to filter known volumes of river water (Section 10300 C; APHA, 1998). (AFDW can be determined from the samples discussed in the next paragraph.) Four samples of known volume will be collected on GF/F filters and stored in 50 cc centrifuge tubes on ice (*not* frozen). **Equal volume of water must be filtered on to each of these filters.** Do not fold. Vacuum on the filters will be kept below 9.0 inches Hg to prevent cell rupture and loss of their contents into the filtrate (Wetzel and

Likens, 1991). At the Water Laboratory in Helena, two of the filters (for C & N analysis) will be placed on a filter holder and rinsed with 10% HCl until they stop fizzing, to remove inorganic carbonates (Niewenhuize et al., 1994). 50 ml tap water will then be pulled through them to remove the acid, and then they will be dried at 105 °C. The remaining two filters (for P analysis) will be dried directly.

For phytoplankton Chl *a* and AFDW, known volumes of water — which should match the same volume used for the CNP filters— from the shaken carboy will be filtered on to 2 different GF/F filters until a distinct green color is observable on each filter. Vacuum must be held below 9 inches Hg. Filters are folded in half (green side in), put in centrifuge tubes & frozen (dry ice).

3.6 Meteorological Measurements

An independent weather station unit will be installed by DEQ within the Fort Keogh Agricultural Experiment Station, on an island immediately adjacent to the river, near Miles City. The station will measure wind speed and direction, air temperature, and relative humidity and will be used to establish a suitable record for statistical correlation of microclimate, if correction is necessary. The weather station will be of research grade quality, with the following specifications:

1. Air temperature accuracy of ± 0.5 degrees C.
2. Relative humidity accuracy of ± 5 percent.
3. Wind speed accuracy of ± 0.5 m/s.

A Hobo Onset or equivalent station is being purchased by DEQ for the project. Data collected from the DEQ weather station will be compared to the NOAA-FAA data provided by the Miles City Municipal Airport (WBAN 24037, COOP ID 245690) to identify the relative usefulness of data outside of the stream corridor. The sites are approximately one mile away from another.

3.7 Hydrologic Measurements

Discharge will be measured by DEQ at a number of sites during the August and September sampling events to establish the hydrologic balance for the project reach. A calibrated Marsh-McBirney current meter and top-setting wading rod or sounding weight will be used to carry out the velocity-area method (Rantz et al., 1982). Because there will be a combination of wadeable- and boat-accessed measurement points, the procedure for collecting discharge for each type of measurements is shown below.

A. Procedure for Wading Discharge Measurement. See Field Procedures Manual, page 30 (G:\WQP\QA_Program\3_Standard Operating Procedures\2-Field Procedures Manual). In this project, we will determine flow using either (1) the 0.2 and 0.8 measurement points at each subtransect, or (2) the 0.6 depth measurement point, depending on site-specific evaluation of the degree of laminar flow at the site. Sites with even laminar flow *and* limited bottom roughness can be measured using the 0.6 method.

B. Procedure for Boat Discharge Measurements. Visual shoreline references (trees, rocks, bushes, etc.) on each bank, along with a 3X6 ft painted plywood—target||board

attached to a post, will be used to assure that measurements are collected along a transect perpendicular to flow. The boat will be positioned to measure depths and velocities by moving to each equidistant point (transect width \div 20) along the transect, and then anchoring in place. A range finder will be used to measure the distance from the boat to the on-shore target board, and a hand-held GPS unit will be used to record the lat and long of the channel midpoint and wetted edges. If the maximum depth in the cross section is less than 3 m and the velocity is low, a rod may be used to measure the depth and support the current meter. For greater depths and velocities, a cable suspension with reel, boat boom, and sounding weight will be used. The Marsh McBirney current meter will be lowered to positions 0.2 and 0.8 of the site depth, and the velocities recorded at each. **If a transect of the Yellowstone River is a combination of boat and wadeable measurements, all points of velocity measurement will be made using the 0.2 and 0.8 method.**

Note: Boat measurements are not recommended where velocities are slower than 0.3 m sec⁻¹ or when the boat is subject to the action of wind and waves.

Field staff will observe any rapids along the study reach, as shown on the BLM Yellowstone River Floater's Guide maps, to ascertain if the rapid provides significant re-aeration. For those with significant re-aeration, a water surface slope between upstream and downstream of the rapid will be taken using the laser level, and spot-check DO measurement will be made using the YSI 85 up- and downstream of the rapid.

Digital photographs of the discharge measurement transects will be taken at each site and latitude, longitude and elevation of the sites will be recorded using a hand-held GPS unit. *Canal return points will only be sampled if definable return points can be identified.*

DEQ will use data acquired as part of the USGS's routine monitoring program. USGS has been contacted to ensure that the stations necessary to complete the 2007 field study will be in operation during the 2007 monitoring period (personal communication; P. McCarthy, 2006). USGS data will be acquired in sub daily increments and will serve as the up- and down-stream boundary conditions for the modeling study reach. The following USGS stations will be utilized:

- (1) USGS 06295000 Yellowstone River at Forsyth, MT (Upstream)
- (2) USGS 06309000 Yellowstone River at Miles City, MT
- (3) USGS 06308500 Tongue River at Miles City, MT
- (4) USGS 06327500 Yellowstone River at Glendive, MT (Downstream)

3.8 Hydraulic Measurements

3.8.1. Dye Tracer Study

See Montana DEQ Field Procedures Manual Section 11.5 Fluorometers (<http://www.deq.mt.gov/wqinfo/monitoring/SOP/pdf/11-05.PDF>), Hubbard et al. (1982). The following procedures, if undertaken, will be carried out by the USGS. The exact locations of the

dye study are in flux because multiple Bureaus within DEQ are cooperating to try to fund the study (see memo, Appendix A). Therefore, the following should be taken as a general plan that will be further refined in the future.

Procedure for Dye Tracer Study A hybrid between the high and low level study approaches proposed by Hubbard et al. (1982) will be completed on the Yellowstone due to the fact that a number of public water supplies are present in the study reach (Forsyth, Miles City and Glendive). The high level approach monitors the dye concentrations at the public water supply intakes to insure that the concentration of dye is less than the maximum levels recommended on the product label while the low level approach fails to do so. It also determines: (1) the travel time of the centroid of dye throughout the modeled reach (using fluorometric techniques) and (2) longitudinal dispersion characteristics of the river by assessing the rate at which the river dilutes the dye. USGS currently maintains two Self-Contained Underwater Fluorescence Apparatus (SCUFA) from Turner Designs in the Helena office. These are proposed for use in the Yellowstone study. Each instrument has a detection limit is 0.04 µg/L for Rhodamine WT dye, provides automatic temperature compensation, and will internally log 11,000 data points at user-defined intervals. SCUFA instrumentation will be leapfrogged in the downstream direction to capture the leading and trailing edges of the dye plume, as well as the peak concentration.

Three unique subreaches will be evaluated as part of the study: (1) Forsyth Bridge (above the diversion) to the Tongue River, (2) Tongue River to the Powder River, and (3) Powder River to the Pacific Railway Bridge in Glendive. Dye will be introduced upstream of Forsyth Bridge at the Myer's Bridge FAS (approximately 47 miles upstream of Forsyth) to ensure complete lateral mixing as well to adequately dilute concentrations prior to arrival at the Forsyth water intake. A single mid channel addition of dye will be used (i.e., 20 liter container of concentrated dye). Length for lateral mixing is calculated as a function of estimated flow velocity (U), channel top width (W), and lateral dispersion coefficient (E_{lat}) for a given flow regime (Hubbard et al., 1982; Chapra, 1997). Lateral mixing distance for the Yellowstone at this site is approximately 40 km

$$L_m = 0.1 \frac{UB^2}{E_{lat}} \quad (2)$$

Rhodamine WT is the preferred dye for tracer studies (Hubbard et al., 1982; Mills et al., 1986; USGS SMIC, 2005), and has been selected for use in this study. Criteria recommended by the Environmental Protection Agency Federal Register Vol. 63, No. 40, National Sanitation Foundation (NSF) Standard 60, and USGS Water Resources Division (Wilson et al., 1986; USGS SMIC, 2005) are 10 µg/L Rhodamine WT for the source water entering a public water supply (prior to treatment and distribution) and 0.1 µg/L in the distribution system. Montana does not have a water quality standard for Rhodamine WT. For this study DEQ will maintain the concentration of Rhodamine WT at or below the levels recommended by the EPA and label instructions. In order to determine the volume of dye necessary to satisfy an adequate endpoint concentration at Glendive, the concentrations at each of the water intakes (Forsyth and Miles City) needs to be determined first to ensure the intakes are protected, and then that the downstream detection limit is satisfied.

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A desired endpoint of 0.25 µg/L near Glendive (well above the SCUFA detection limit of 0.04 µg/L) was identified by DEQ to ensure that photodegradation, biodegradation, adsorption to sediments, or uptake by plants do not cause concentrations to fall below the analytical limits. Smart and Laidlaw (1977) and Turner et al. (1991) indicate that Rhodamine WT is conservative in studies of one week of duration or less (98-100% recovery). Other studies (e.g., Hubbard et al., 1982) indicate significant loss. A margin of safety was therefore selected to ensure detection while still maintaining concentrations well below the EPA, NSF and USGS criteria of 10 µg/L at public water supply intakes. The necessary volume of a 20% Rhodamine WT dye solution required to satisfy these requirements is calculated as follows (Hubbard et al., 1982):

$$V = 2 \cdot 10^3 \cdot \frac{Q_m L}{U} \cdot C_p^{0.93} \quad (3)$$

Where: (V) is the volume of dye in liters, (Q_m) is the expected or actual discharge in the reach in cubic meters per second, (L) is the distance from injection to sampling point in km, (U) is the mean velocity in m/s, and (C_p) is the peak concentration desired in µg/L. Based on these calculations, a 20 L injection of Rhodamine WT 20% solution near the Myer's FAS (upstream of Forsyth) will achieve the 0.25 µg/L target at Glendive for average August-September flows. These values, of course, will need to be—fine-tuned|| as real-time flow data near the time of the field study are compiled. Estimated dye concentrations at critical points in the study reach (e.g. water intakes) are shown in Table 3.2. They are nearly a factor of 10 below the EPA, NSF, and USGS recommended values.

Table 3.2. Estimated Dye Concentrations at Specific Locations along on the Yellowstone River (August-Sept flow regime)

Hydraulic Reach	Upstream Point	Downstream Point	DS Reach Stationing (km) ⁽¹⁾	Mean Q (m ³ /s)	Mean U (m/s)	Concentration (µg/L)
BOUNDARY	---	Myer's FAS	0	205	---	---
NA-MIXING	Myer's FAS	USGS @ Forsyth	75.5	205	0.91	1.15
YLW-01	USGS @ Forsyth	USGS @ Miles City	128.7	230	0.91	0.65
YLW-02	US Tongue River	US Powder River	201.5	235	0.89	0.40
YLW-03	US Powder River	Glendive RR Bridge	310.7	240	0.89	0.25
Total Dye Rhodamine WT (20% solution)			20 liters			

⁽¹⁾ McCarthy (2006); DEQ (2006).

⁽²⁾ Unknown Reach Length

3.8.2 Channel Dimensions and Related Measurements

Procedure for Velocity and Depth Rating Curve Development. Depth and velocity measurements (in the form of a rating curve) are used to calculate travel time as well as wetted channel dimensions in QUAL2K. DEQ will measure these values in the field to provide model input as well as validation information. At each of the mainstem sites where discharge will be measured (Section 3.7), mean cross-sectional velocity, mean depth, and wetted river width data will already be available. At other specified sites (Appendix C; benthic/rate sites), mean river depth and wetted width will be measured to define the overall hydraulics of the system. Mean river depth will be determined from 11 measurements along each transect site. Wetted width will be measured using a laser range finder. In addition, field measurements from USGS at USGS-gauged sites will be used. Digital photographs of the river at each physical characteristic

measurement location will be taken in the up- and down-stream directions. Latitude, longitude and elevation of the sites will be recorded using a hand-held GPS.

One low-head dam is present within the study reach (Fischer, 1999; USFWS, 2002). The Cartersville Diversion Dam (also called Forsyth Diversion Dam) is located near Forsyth and was constructed during the early 1930s utilizing riprap capped with concrete. The dam is over 800 feet in length and spans the entire width of the channel. In order to adequately define velocity and flow depth resulting from this structure, as well as to compute reaeration (Chapra, 2003), height of the diversion dam is a necessary input to QUAL2K for weir computations.

Two measurements will be made at the Forsyth low-head dam (if possible) to identify the average height of the dam: one at the left bank, and one at the right.—As built drawings will also be consulted. The mean of the left and right banks will be used to determine the average weir height. A metric fiberglass survey rod (or engineers tape) will be used to record this measurement. Digital photographs will be taken of the structure and the latitude, longitude and elevation will be recorded using a hand-held GPS. Width will be measured using a laser range finder and will be compared to values measured from aerial photography.

3.9 Boat Usage

Equipment. Because of the river's depth, a boat will be used for collecting a large number of the measurements outlined above. We will use a 16 ft Jon boat (mod-V hull with tunnel) equipped with an outboard jet. The Jon boat provides a relatively stable platform from which to work, e.g., operating a small winch/boom apparatus to collect benthic samples or measure velocity. Additional equipment for the boat are:

1. Coast Guard approved life preserver for each occupant
2. Two type-IV throwable floatation device
3. Horizontally-mounted fire extinguisher (for fires type A, B and C)
4. Airhorn
5. Flares (visual distress signal)
6. Oars
7. Bailing device, including a bilge pump
8. Winch/boom apparatus for benthic grabs, velocity measurements, etc.
9. Claw-type anchor and mushroom-type anchor with chain and rope
10. Large cleat on bow to secure anchor line
11. Electric anchor cable winch

Boat Operation and Safety Training. **All field staff in the boat will be required to wear their life preserver at all times.** All project participants who will operate the boat have completed a boating safety class offered by the U.S. Coast Guard Auxiliary. A copy of the Coast Guard textbook from the course (USCG 2006) will be carried to the field and kept in the boat. Montana boating regulations available at: <http://fwp.mt.gov/fishing/regulations/boatrestrictions.html> will be reviewed by all project participants who will be in the boat. Participants who will operate the boat will familiarize themselves with the boat & motor operation on a lake or reservoir prior to using the boat on the Yellowstone River.

Intended Usage of Boat. The boat will be launched as close as is reasonably possible to each sampling site. The boat will be anchored in place at points where measurements (velocity, water samples, etc.) are made along transects. One individual on the boat will be assigned as a lookout for other boats on the river at times when the boat is anchored in the river.

4.0 Sample Handling Procedures

Sample storage times are shown in Table 4.0 of the DEQ WQPB QAPP (DEQ 2005). Standard DEQ Water Quality Planning Bureau site visit/chain of custody forms will be used to document and track all samples collected in the project. Samples will be delivered to the Department of Public Health and Human Services Environmental Laboratory (DPHHS laboratory) in Helena, or shipped frozen (or delivered) to the UM Flathead Lake Biological Station. The following samples will be delivered to the Flathead Lake Biological Station for analysis: DIC, dissolved methane (if collected), total N, total P, NO_{2+3} , total NH_3 , DON, DOP, SRP, seston CN samples, seston P samples, phytoplankton Chl *a* & AFDW samples. The DPHHS laboratory will receive benthic Chl *a* samples, and SSC and turbidity samples.

5.0 Laboratory Analytical Measurements

The detection limits of the analyses undertaken by the DPHHS laboratory are detailed in Table 4.0 of the DEQ WQPB QAPP (DEQ 2005). For nutrients and other water quality parameters listed in Table 2.1 of this SAP to be analyzed by the Flathead Lake Biological Station, method detection limits are as shown in Table 5.1, below. Table 5.2 (below) shows the performance characteristics of measurements made by the YSI 6600EDS sondes (YSI, 2006).

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Table 5.1. Major Plant Nutrients and their Detection Limits, As Analyzed by the Flathead Lake Biological Station.

Parameter	Units	Analytical Method	Sample Prep/holding time	Detection Limit	Method Reference #
Dissolved inorganic carbon (DIC)	mg/L	Phosphoric acid injection	Filtered asap, stored at 4 degC/ 14 days	0.04 mg/L	13
Total nitrogen (TN)	µg/L	Persulfate digestion	Frozen asap/ 6 months	20 µg/L	7, 8, 9, 10
Nitrate + nitrite (NO ₂₊₃)	µg/L	Cadmium reduction	Filtered and frozen asap/ 6 months	0.6 µg/L	3, 4
Dissolved organic nitrogen (DON)	µg/L	Persulfate digestion	Frozen asap/ 6 months	17 µg/L	
Total ammonia (NH ₃)	µg/L	Automated phenate method	Filtered, frozen asap/ 6 months	5 µg/L*	5, 6
Total phosphorus (TP)	µg/L	Sulfuric acid & persulfate digestion followed by ascorbic acid	Frozen asap/ 6 months	0.4 µg/L	1, 2
Dissolved organic phosphorus (DOP)	µg/L	Sulfuric acid & persulfate digestion followed by ascorbic acid	Frozen asap/ 6 months	3 µg/L	
Soluble reactive phosphate (SRP)	µg/L	Direct ascorbic acid	Filtered, frozen asap/ 6 months	0.3 µg/L	1, 2

* As a result of background ammonia on field filter blanks, the practical detection limit may be approximately 20 µg/L.
All the automated methods are done on a continuous flow instrument (Technicon™ Autoanalyzer™ II)

Method References:

- 1) Standard Methods for the Examination of Water and Wastewater, 17th Edition (1989), p.4-177 Method 4500-P E. and p. 4-170 Method 4500-P B.
- 2) Technicon Autoanalyzer II Industrial Method No. 155-71W Ortho Phosphate in Water and Seawater, adapted (Ted Walsh, U. of Hawaii, Personal communication, 1988).
- 3) Standard Methods for the Examination of Water and Wastewater, 16th Edition (1989), p.4-135, Method 4500-NO3- E.
- 4) Technicon™ Autoanalyzer™ II Industrial Method No. 158-71W/B, revised Aug 1979.
- 5) Standard Methods for the Examination of Water and Wastewater, 17th Edition (1989), Method 4500 H. pg 4-111 - 4-128.
- 6) Technicon™ Autoanalyzer™ II Industrial Method No. 154-W/B, revised January 1978, Ammonia in Water and Seawater.
- 7) D'Elia, C.F., P.A. Steudler, and N. Corwin, Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 1977. 22:760-764.
- 8) Solorzano, L. and J.H. Sharp. Determination of total dissolved nitrogen in natural waters. Limnol. Oceanogr. 1980. 25(4):751-754.
- 9) Standard Methods for the Examination of Water and Wastewater, 16th Edition (1985), p.400, Method 418 F.
- 10) Technicon Autoanalyzer II Industrial Method No. 158-71W/B, revised Aug 1979.
- 11) Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998). P5-20 or 5-24, Method 5310 B or D.
- 12) Menzel, D. W. and R. F. Vaccaro. 1964. The measurement of dissolved organic and particulate carbon in seawater. Limnology and Oceanography 9:138-142.
- 13) Operating Procedures Manual for Oceanography International Corporation Total Carbon Analyzer.

Table 5.2. Performance Characteristics of the YSI 6600EDS Sonde

Parameter	Resolution	Accuracy	Range
Water Temperature	0.01 ° C	± 0.15 ° C	-5 to 45 ° C
pH	0.01 units	± 0.2 units	0 to 14 units
DO (mg/L)	0.01 mg/L	± 0.2 mg/L	0 to 50 mg/L
DO (% saturation)	0.1% air sat.	± 2%	0 to 500% air sat.
Specific Conductance	0.001 mS/cm	± 0.5% of reading	0 to 100 mS/cm
Chlorophyll a	0.1 µg Chl a /L	none given*	0 to 400 µg Chl a /L
Turbidity	0.1 NTU	2 NTU	0 to 1000 NTU
Battery Life	90 days at 20 ° C, 15 min logging intervals w turbidity and Chl a on.		

*In vivo measurements will only be as accurate as the laboratory samples against which they are calibrated.

6.0 Quality Assurance and Quality Control Requirements

Quality assurance and quality control (QA/QC) requirements for some of the more unique procedures in the SAP (e.g., benthic SOD chambers, long-term YSI sonde deployment) have been outlined in the project QAPP. All other standard QA/QC requirements followed by DEQ (DEQ 2005) will be instituted for this project.

7.0 Data Analysis, Record Keeping, and Reporting Requirements

Data logged in the YSI 6600EDS sondes will be downloaded to a DEQ computer via the EcoWatch for Windows program provided by YSI. Data generated during this project will be stored on field forms, in laboratory reports obtained from the laboratories and in Excel spreadsheets hosted by DEQ shared network servers (backed up on a daily basis). Site Visit/Chain of Custody forms will be properly completed for all samples. Written field notes, field forms (photo log, site information), and digital photos will be processed by DEQ staff following QA/QC procedures to screen for data entry errors. Data provided by the DPHHS laboratory and the Flathead Lake Biological Station will be in a SIM-compatible format, and will be readied for import into the DEQ's local STORET database and EPA STORET database by the Montana Department of Environmental Quality. Data will be processed with Excel and with Minitab release 14, Systat version 10 or StatMost for Windows statistics utilities. ArcView version 9 ArcMap will be used for GIS applications. The GPS coordinate system datum will be NAD 1983 State Plane Montana, in decimal degrees, to at least the third decimal (thousandths). All data generated during this project will be available to the public.

8.0 Schedule for Completion

Equipment purchases have proceeded since late 2006. Boating safety and first aide courses were completed by project participants in spring 2007.

Five major trips are scheduled for completing this SAP:

- 1) Deployment of YSI sondes in late July/early August 2007 (approximately 8 days)
- 2) Sampling run No. 1 (calibration dataset), 3rd and 4th full weeks of August, 2007 (approximately 10-12 day trip)
- 3) Check and clean YSI sondes of biofouling, end Aug/start Sept, 2007 (approximately 5 days)
- 4) Sampling run No. 2 (validation dataset) 3rd and 4th full weeks of September, 2007 (approximately 10-12 days).
- 5) Retrieval of YSI sondes, late September/early October 2007 (approximately 5 days).

The model and its associated report should be completed by May 2008. Further refinement of the model based on the dye study will be completed after USGS provides the dye study results.

9.0 Project Team and Responsibilities

This project is intended to be carried out by staff of the Montana Department of Environmental Quality. Personnel directly involved in this project are presented in Table 9-1.

Table 9.1. Project Personnel Responsibilities.

Name	Organization	Project Responsibilities
Michael Suplee	MT DEQ	Project Management/data collection
Kyle Flynn	MT DEQ	Model Calibration and Validation
Michael Van Liew	MT DEQ	Model Calibration and Validation
Monitoring Staff 1	MT DEQ	Data Collection
Monitoring Staff 2	MT DEQ	Data Collection

11.0 References

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Appendix A

Memo

To: Jon Dilliard, Bonnie Lovelace, George Mathieus, Todd Teegarden
From: Michael Pipp, Bob Bukantis, Mike Suplee, Kyle Flynn, and Jim Stimson
CC: Joe Meek, Mark Smith, Kate Miller
Date: April 19, 2007
Re: Potential Cooperative Project Opportunity with the USGS

Proposal Overview

The U. S. Geological Survey (USGS) is interested in conducting a dye -tracer study on the Yellowstone River. A study of this kind would be extremely helpful to several DEQ programs and projects. To undertake the study the USGS needs cooperators to help with funding. The USGS would conduct the study and would participate in funding the effort using their own matching funds. They would match funding from other cooperators on a 40:60 ratio. The purpose of this memo is to explain how the proposed dye -tracer study provides critical information for several DEQ programs and to solicit input on possible funding sources from DEQ Bureau Chiefs and Section Managers. An estimate of the cost for the study is being developed at this time through discussions with the USGS and DEQ staff listed above. As soon as estimates are available Michael Pipp and Bob Bukantis will request a brief meeting with you all to discuss funding possibilities.

Dye-Tracer Study and Numeric Nutrient Criteria Development

The Water Quality Standards Section is developing numeric nutrient criteria for all surface waters of the state. Starting in summer 2007, The Section is planning to work in the lower Yellowstone River in order to develop criteria for the lower river. The Section is planning to use a water quality model (QUAL2K) to answer the following question:

In a segment of the lower Yellowstone River, what are the highest allowable concentrations of nitrogen and phosphorus which will not cause benthic algae to reach nuisance levels and/or dissolved oxygen concentrations to drop below applicable State water quality standards?

The highest input of nitrogen and phosphorus concentrations that do not cause nuisance algae growth and/or exceedences of the DO standards under low -flow conditions may be used as the numeric nutrient criteria for this river segment. Our basic assumption is that the underlying mechanistic foundation of the model is sound, but direct measurement of key parameters driving the model will increase the model's accuracy.

Dye-Tracer Study and Nutrient Water Quality Model

Water-quality models are typically no better than the travel time used in their mass transport formulation and several approaches have been proposed in the literature for estimation of reach travel time. The most accurate of these is through dye-tracer and fluorescence studies, of which MDEQ is proposing for the Yellowstone River. Accurate travel time is crucial in calculating water temperature within the model (i.e. water temperature is extremely sensitive in DO modeling), for correcting temperature dependent rate coefficients, and completing calculations for which a particular segment is influenced by those rate coefficients. Several unique subreaches are proposed as part of the dye-tracer study for the modeling effort. These include: (1) Forsyth Bridge to the Tongue River, (2) the Tongue River to the Powder River, and (3) the Powder River to the Pacific Railway Bridge in Glendive. It is believed that the proposed dye-tracer study could be extended upstream (to Billings for example) to characterize travel time/dispersion for public water supply/drinking water purposes.

Dye-Tracer Study and Surface Water Public Water Supplies

In 2004 the Source Water Protection Program wrote a grant to EPA to help fund a USGS study that used flood wave velocity to estimate surface water time of travel along a portion of the Yellowstone River. It was hoped that the flood wave study could be used as a—quick and easy|| method to estimate time of travel for the purpose of assessing the potential impact of contaminant spills or releases on public water supplies along the Yellowstone. However, the flood wave study's conclusions and results can only be validated with the aid of a dye-tracer study as described above. In addition to validating the flood wave study, time of travel and dispersion data generated by the proposed dye study would give the Public Water Supply and the Source Water Protection programs additional information to help assess the threat of potential contaminant spills or releases on the river. The information from the proposed study can be used to better estimate: 1) how long it will take a contaminant plume to reach a public water supply from a give release site, 2) how long it will take for the plume to pass by the water supply's intake, and 3) the peak concentration that can be expected in the vicinity of the surface water intake. Funding the proposed dye-tracer study would help multiple programs within DEQ.

Appendix B Equipment List

ITEMS FOR WATER SAMPLING

- Field Sheets, Write in Rain Level Survey Book, Labels, Clip Board, Sharpie Pens/pencils
- Plastic Carboys (2)
- 0.45 µm filter cartridges
- 60 cc syringes (clean; 25)
- Sample Containers (includes duplicates and extra bottles, and bottles for chamber fluxes)
 - Water sample bottles (develop detailed list)
 - Centrifuge tubes or petri dishes for Chl *a* (benthic and phytoplankton) and CNP samples
 - 1 gallon size ziplock bags
- Preservatives
 - H₂SO₄
 - Formalin (100 ml)
- 47 mm GF/F filters and tweezers
- 47 mm filter apparatus
- Hand vacuum pump
- Centrifuge tubes
- Aluminum foil
- Ice Chests (3) and Ice
- Dry ice
- Portable 12 v/120 v freezer
- DH 48 and associated bottle
- DH 95 boat or bridge mounted sampler, and associated bottle
- Large HDPE plastic jar as an acid bath for DH48 bottles

ITEMS FOR DO WINKLER TITRATIONS

- Manganese sulfate solution
- Alkalie-Azide reagent
- Standard sodium thiosulfate titrant
- Starch indicator solution (eye dropper)
- 10% HCl solution
- DI water
- Concentrated H₂SO₄
- Carboy for waste chemicals (1)
- 100 ml volumetric pipette (2) and bulb
- 50 ml burette with stop-cock
- Ring stand and burette clamp
- Stirrer plate
- 250 Erlenmeyer flasks (4) and stirrer rods
- Ice chest and ice
- 300 ml dark BOD bottles (9) and holder caps
- 300 ml light BOD bottles (9) and holder caps
- Rack to hold BOD bottles (2)

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- Lind (1979) book

ITEMS FOR REAL-TIME WATER QUALITY

- Calibrated YSI 6600ED sondes (8)
 - Calibration Solutions (pH)
 - Spare Batteries
 - Clamp for YSI sonde (3.5—grip)
- YSI deployment apparatus (8)
- SS cable (minimum of total 1,250 ft; can be in roles of 150 or 200 ft)
- Swage tool and swage locks
- Cable cutter
- Shovel
- Heavy blocks with eyebolt for non-bridge deployment
- Laptop with Ecowatch
- Laptop-to-sonde cable
- 650 hand-held YSI with barometer
- 650-to-sonde cable
- Boat hook with special hook on end to catch cables
- HOBO temperature loggers (6)
- Fence posts or bricks to hold data temp loggers
- Zip ties
- Small sledge hammer

ITEMS FOR SAMPLING FROM BOAT/FLOW

- Top Setting Rod (2)
- Marsh McBirney Velocity Meter (2)-lab calibrated (set to m sec^{-1})
- Laser-level, tripod and batteries
- Bushnell Laser Range Finder
- Grey painted plywood—target|| (4' X 6') and fence posts (2)
- Fiberglass survey rod
- Long fiberglass tape (m)
- GPS Unit and batteries
- Hip waders and boots
- Marsh McBirney boat/bridge mountable velocity device
- Ponar grab

ITEMS FOR SOD MEASUREMENT

- Benthic chambers (2)
- 500 GPH pumps (2) and 1800 GPH pumps (2)
- 100 ft special water-tight connector extension cords (2)
- Honda generator
- Safety breaker (110 v)
- Length of heavy chain (2)
- Snorkel and mask, bathing suite and Tevas
- 300 ml dark BOD bottles (6) and caps
- Ice chest (1)

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the
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- YSI 85 (2)
- 60 cc syringe (8)-need 10% HCl and DI water rinse between sites

BOAT SPECIFIC ITEMS AND GENERAL ITEMS

- PFDs for each person
- Oars
- Bailing device, additional to bilge pump
- Winch/boom apparatus for benthic grabs, velocity measurements, etc.
- Claw-type anchor and mushroom anchor with chain and rope
- Sea Anchor
- Rope (200 feet)
- Bimini and boat cover
- Grease gun
- 2-cycle oil (4 qts)
- Extra 12 v batteries (2)
- Large cleat on bow to secure anchor line

- Wilderness First Aid kit
- USCG book, First Aid book
- Cell Phone
- Digital Camera
- Calculators
- Electronic depth finder
- 5-10 gallons gasoline
- Weather Station (for initial deployment)

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Appendix C. List of activities to be completed at each site. After completing an activity, place an X in the circle. Include dates where indicated.																										
SITE NAME	Sampling Trip No.	Depth/width integrated Water Samples					Grab Water Samples			Benthic Chambers			Activities to Complete For Sample Run 1, 2				Rate Measurements		Channel Dimensions				These activities occur on trips prior to and after sampling runs 1, 2			
		Nutrients (dissolved, total)	SSC & turbidity	TIC (DIC)	Phyto Chl a	Seston CNP	Nutrients (dissolved, total)	SSC & turbidity	TIC (DIC)	SOD	WOD (Winkler)	Ammonia & DIC flux	Benthic Chl a (11 trnscts)	% bottom with heavy algae cover (11 trnscts)	% bottom with matching SOD conditions	PERI-1	Phyto photosynthesis, light/dark bottles (Winkler)	Photosynthesis of Cladophora (YSI 85)	YSI 85: Cross-check sondes	Mean Depth	Wetted Width	Flow	Low-head dam dimensions	YSI 6600 EDS sondes: Long-term deploy. In, out	Temperature (HOBO logger) in, out	Weather Station in, out
Yellowstone River Sites																										
Buffalo Mirage FAS	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>									<input type="radio"/>				<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date in: _____		
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>									<input type="radio"/>				<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date out: _____		
Rosebud (West Unit) FAS	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>		<input type="radio"/>		<input type="radio"/> Date in: _____			
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>		<input type="radio"/>		<input type="radio"/> Date out: _____			
Far West FAS	1									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date in: _____		
	2									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date out: _____		
Upstream of Cartersville Canal return flow	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date in: _____			
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date out: _____			
Ft. Keogh Bridge, w/s of Tongue R.	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date in: _____	<input type="radio"/> Date in: _____	
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date out: _____	<input type="radio"/> Date out: _____	
Rosche Jaun FAS	1																<input type="radio"/>				<input type="radio"/>					
	2																<input type="radio"/>				<input type="radio"/>					
Piogue Island State Park	1									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date in: _____	
	2									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date out: _____	
Kinsey Bridge FAS	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>					<input type="radio"/> Date in: _____		
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>					<input type="radio"/> Date out: _____		
Bonfield FAS	1									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date in: _____	
	2									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date out: _____	
Upstream of Power R. confluence & Shirley Main Canal return	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date in: _____			
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date out: _____			
Terry Bridge	1									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date in: _____	
	2									<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>				<input type="radio"/> Date out: _____	
Upstream of O'Fallon Creek	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date in: _____			
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date out: _____			
11 miles w/s of Glendive (Floaters Guide river mile 445)	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date in: _____			
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>		<input type="radio"/> Date out: _____			
Old Bell Street Bridge, Glendive	1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date in: _____		
	2	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>												<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				<input type="radio"/> Date out: _____		
Tributaries & Irrigation Canals																										
Cartersville Canal at withdrawal	1																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Rosebud Cr. confluence w Yellowstone	Opportunistic						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
							<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Cartersville Canal return point	1						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Tongue R., confluence w Yellowstone	1						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Kinsey Main Canal at withdrawal	1																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Shirley Main Canal withdrawal	1																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Kinsey Main Canal return point	1						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Shirley Main Canal return point	1						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Powder R., confluence w Yellowstone	1						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Terry Main Canal at withdrawal	1																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	2																			<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Terry Main Canal return point 1	Opportunistic						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
Terry Main Canal return point 2	Opportunistic						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
O'Fallon Cr. confluence w Yellowstone	Opportunistic						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>											<input type="radio"/>	<input type="radio"/>	<input type="radio"/>				
	Opportunistic																									
	Opportunistic																									
Waste Water Treatment Plant Effluent																										
Forsyth WWTP	Access pending						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>													<input type="radio"/>				
Terry	Access pending						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>													<input type="radio"/>				
Miles City WWTP	Access pending						<input type="radio"/>	<input type="radio"/>	<input type="radio"/>													<input type="radio"/>				

Appendix D. Field Forms Specific to the Yellowstone Modeling Project

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Date (m/d/y): _____

Table 1. Benthic & Algae Cross-Section Data, and Near-bottom Velocity Values.

Transect Locale	Channel Dimensions & Substrate			Benthic Chlorophyll <i>a</i>			Near-bottom River Velocity [‡]	
	Dist. from wet edge	<i>Channel Wet Width:</i>		Method (Hoop-H,	Means (boat-B,	Estimated bottom cover	Velocity	Means (boat-B,
	(m)	Depth (cm)	Substrate Size (mm)*	Core-C, Template-T)	wading-W)	by visible algae (%) [†]	(m sec ⁻¹)	wading-W)
A (Left wet edge)								
B								
C								
D								
E								
F (midchannel)								
G								
H								
I								
J								
K (Right wet edge)								

* If smaller than sand, write "SILT", if hardpan, write "HP". [†] If river bottom not visible, write "INV".

[‡] Take velocity measurement as near to the river bottom as practicable.

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Appendix D2. Yellowstone Modeling Project: Sediment Oxygen Demand and Solute Flux Field Form

Activity ID: _____ Site Name: _____ Date (m/d/y): _____

Table 1. SOD

Benthic Chamber	Measured Near-bottom veloc. (m sec ⁻¹)	Water Depth (cm)	Dominant Substrate Class*	Date:		Starting Conditions: YSI 85		Intermediate DO checks (YSI 85)						Incubation End Time	End Date (m/d/y)	Ending Conditions: YSI 85	
				Incubation Start Time		Temp (° C)	DO (mg/L)	No. 1 Time	DO (mg/L)	No. 2 Time	DO (mg/L)	No. 3 Time	DO (mg/L)			Temp (° C)	DO (mg/L)
Chamber A:																	
Chamber B:																	

* Clay/Silt (FN), Sand (SA), Gravel-fine (GF), Gravel-coarse (GC), Cobble (CB), Boulder (BL), Hardpan (HP)

Table 2. Solute Fluxes

Benthic Chamber	Solute Flux	Start Date	Start Time	Start Sample Volume (ml)	End Date	End Time	End Sample Volume (ml)
Chamber A:	DIC						
	Ammonia						
Chamber B:	DIC						
	Ammonia						

Table 4. Percent of stream cross-section with equivalent SOD

Overall proportion of X-section with similar substrate*: _____

Overall proportion of X-section with similar velocity*: _____

Estimated % Cross-Section With Equivalent SOD: _____

* Refer to 'Benthic & Algae Cross-Section Measurement Form' for individual values of A through K along the transect.

Table 3. WOD via Winkler Titrations

Dark Bottle		Time Sample Fixed	Date Sample Fixed	Normality of sodium thiosulfate titrant	Volume sodium thiosulfate titrant (ml)	Volume of Sample Titrated (ml)	DO (mg/L)	Date Sample Run	Thiosulfate Titration	
Replicate	Bottle No.								Start Vol. (ml)	End Vol. (ml)
1 Initial										
1 repeat measure										
2 Initial										
2 repeat measure										
3 Initial										
3 repeat measure										
1 Final										
1 repeat measure										
2 Final										
2 repeat measure										
3 Final										
3 repeat measure										

Using a Computer Water-Quality Model to Derive Numeric Nutrient Criteria for a Segment of the Yellowstone River

Appendix D3. Yellowstone Modeling Project: Light/Dark Bottle (phytoplankton productivity) Field Form

Activity ID: _____

Site Name: _____

Date (m/d/y): _____

Table 1. Light Bottles, Winkler Titration

Light Bottle		Incubation Start Time	Incubation End Time (bottle fixed)	Incubation Date	Normality of sodium thiosulfate titrant*	Volume sodium thiosulfate titrant (ml)	Volume of Sample Titrated (ml)	DO (mg/L) [†]	Date Sample Run	Thiosulfate	
Replicate	Bottle No.									Start Vol. (ml)	End Vol. (ml)
1											
1 repeat measure											
2											
2 repeat measure											
3											
3 repeat measure											

Table 2. Dark Bottles, Winkler Titration

Dark Bottle		Incubation Start Time	Incubation End Time (bottle fixed)	Incubation Date	Normality of sodium thiosulfate titrant*	Volume sodium thiosulfate titrant (ml)	Volume of Sample Titrated (ml)	DO (mg/L) [†]	Date Sample Run	Thiosulfate	
Replicate	Bottle No.									Start Vol. (ml)	Thiosulfate End Vol. (ml)
1											
1 repeat measure											
2											
2 repeat measure											
3											
3 repeat measure											

*1N thiosulfate solution = 1 M.

[†] Based on the formula of Wetzel and Likens (1991):

$$\text{mg O}_2/\text{L} = \frac{(\text{ml titrant})(\text{molarity of thiosulfate})(8000)}{(\text{ml sample titrated})(\text{ml of BOD bottle} - 2 / \text{ml of BOD bottle})}$$

USING A COMPUTER WATER-QUALITY MODEL TO DERIVE NUMERIC NUTRIENT CRITERIA FOR A SEGMENT OF THE YELLOWSTONE RIVER

Sampling and Analysis Plan-Addendum

Prepared for:

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October 24, 2007

Purpose of this Addendum

During the sampling phase of the Yellowstone River project (July 30 -September 23, 2007), several modifications to the original SAP were necessitated by realities encountered in the field. This addendum documents these changes. Each section number below refers to the corresponding section in the original SAP. It is recommended that the reader review the original SAP prior to reading this document. Explanations as to why the change was needed are provided with each.

Section 2.2 Overview of What Will be Measured, Where, and How Often

Modifications to the site locations, and rationales for the changes, are shown in Table 2.1. A further explanation is necessary for the Kinsey Bridge FAS modification (Table 2.1). It was intended that the new site (Yellowstone River @ river mile 375) would completely replace the Kinsey Bridge FAS site. However, dropping water levels during the August sampling event created river hazards for the boat, and therefore the YSI was moved downstream to the Kinsey Bridge FAS (which could be accessed by road). Thus, the dataset for the Yellowstone River zone downstream of the Tongue River & Miles City WWTP is in two parts; data collected at river mile 375 (through August 22nd), and data collected at the Kinsey Bridge FAS (August 22nd-September 19th).

Table 2.1 Addendum. Modification of site locations.

Originally Proposed Site	Modification	Explanation
Yellowstone River @ Kinsey Bridge FAS	Yellowstone River @ river mile 375, 5.5 miles upstream of Kinsey Bridge	The original intent of the Kinsey Bridge site was to detect potential influences from the Tongue River and Miles City WWTP. The modified site (river mile 375) was deemed better because it was closer to these river influences (new site was 4 miles downstream of WWTP, Kinsey Bridge was 9.5 miles downstream).
Yellowstone River upstream of Powder River & Shirley Main Canal confluences	Yellowstone River just upstream of Powder River confluence	Dirt road access to site upstream of Powder River had potential (during rain) to render the site impassable for boat & trailer. Boat was required to get upstream of Shirley Main Canal confluence. YSI could be retrieved from modified site without the boat, if required.
Yellowstone River 11 miles upstream of Glendive	Yellowstone River @ Fallon Bridge FAS	Reaching the Yellowstone River 11 miles upstream of Glendive required either boat travel from Glendive or a local launch site. No local launch was found, and boat travel from Glendive was deemed too hazardous due to rocks and the river's shallowness.

Section 3.1 Sediment Oxygen Demand, Benthic Chambers & Solute Fluxes

Fewer SOD Measurements Completed. SOD measurements turned out to be very time consuming. Further, Steve Chapra (QUAL2K model developer) indicated to DEQ prior to the start of the field sampling that SOD measurements are not the highest priority in overall model development. Therefore, given the large number of project tasks and shortage of time, SOD measurements were collected only at two sites; Far West FAS, and the 1902 Bridge (upstream of Tongue River site), and only for the August (calibration) dataset.

Modifications to SOD Measurement. Measurement of SOD in a river system proved to be very different than what I have experienced in lentic systems. The YSI 6600 sonde dissolved oxygen (DO) data from the first set of duplicated SOD incubations (reviewed in the field) revealed that DO, instead of decreasing over time (as expected), increased instead. As DO increased throughout the day in the river, so too did DO in the chambers. Because the chambers have a skirt that penetrated into the river bottom 10 cm and a second rubber skirt at the sediment/water interface, I believe the DO increase was due to a proportion of river water moving through the coarse gravels of the river bed below the chambers' skirt which then mixed (to some unknown degree) with the water in the chambers. To help control for this, subsequent SOD measurements were carried out with one YSI 6600 sonde in the benthic chamber (experiment) and the other YSI 6600 sonde attached to the outside of the chamber in the flowing river water (control). This arrangement precluded a duplicate chamber incubation because we only had the two YSI sondes available.

Modification to SOD Calculations. A cursory review of the data collected in the modified manner described above showed that DO rose more slowly inside the chambers than outside. Because of this, the time-DO curve generated from each YSI (inside chamber, outside chamber) can be used to estimate SOD. This will be accomplished by determining the difference in the area under the time-DO curve for three scenarios: assuming no mixing of external water with internal chamber water, assuming 50% mixing, assuming 100% mixing. SOD values will be corrected for WOD proportional to each scenario.

Modifications to WOD Measurement. Rather than measure oxygen demand of the water within the chambers (WOD) in triplicate BOD bottles, they were measured in duplicate (two initial and two final dark BOD bottles). This was required due to the limited time available to run replicate measures of WOD within the 3-day holding time.

Other Sediment Fluxes Not Measured. Due to time constraints and the influence of dilution from through-gravel flows into the benthic chambers, we deemed it impractical to measure sediment fluxes of DIC, SRP and ammonia.

Section 3.2. Other Rate Measurements

Light/dark Phytoplankton Productivity Measurements. Light/dark BOD bottles were used to estimate phytoplankton primary productivity. The SAP indicated that water used to fill the light/dark bottles would be drawn from composite water samples composited via the equal-width-increment (EWI) method. We concluded that the process of compositing the water in the carboy would cause too much change in the initial DO concentration of the water sample to make it suitable for the light/dark bottle tests. Instead, the light/dark BOD bottles were filled at the river's surface in good-flowing water. The bottles were carefully filled to avoid gurgling or bubbling so that the initial DO conditions of the river were maintained.

Influence of Drifting Filamentous Algae on DO. Large quantities of drifting filamentous algae (likely *Cladophora* spp.) were observed in the river, and were potentially a strong influence on diel DO patterns. We undertook measurements of the drifting algae at a Yellowstone River site near Miles City. Drifting algae was quantified in two steps. In the first step, small blobs of the drifting filamentous algae were placed in duplicate dark BOD bottles and the change in DO over time was determined. The changes were corrected for the oxygen demand associated with the water fraction in the bottles. The blobs were then frozen for later analysis of dry weight, AFDW and Chl *a*. This provided a DO uptake per unit mass of drifting algae per unit water volume under simulated nighttime conditions. In the second step, a 0.3364 m² screen (built from standard window screening) was placed in the river and allowed to capture filamentous algae that drifted through it. The screen was carefully monitored to make sure that it did not begin to plug and consequently route drifting algae around it. The screen was placed where it extended from the surface to the bottom of the river at a location just upstream of the Miles City USGS gage, so that total river flow at the site would be known. The velocity of the water at the screen was recorded using a Marsh McBirney flow meter. The time of accumulation as well as the total dry weight, AFDW and Chl *a* content of the captured algae was determined. These data will be incorporated into the QUAL2K model to help characterize a DO sink (drifting filamentous algae) not anticipated when the SAP was written.

Section 3.2. Real-Time Water Quality Measurements (YSI 6600EDS)

The sonde deployers built were very similar in design to that shown in Fig. 3.1, except that they were constructed entirely from aluminum and did not have concrete slabs as a component. Also, the YSI sondes were attached directly to the deployers with zipties and were not contained within a PVC pipe as shown. None of the deployers were attached to bridges; instead, they were attached to concrete blocks (140 lbs) located upstream of the deployer by ~60 ft of 1/8" stainless steel cable. All were placed in good flowing water approximately 3-4 ft deep. The YSIs were maintained 10 cm (4") off the bottom when attached to the deployers.

Section 3.5. Water Samples

Modification to Equal-Width-Increment Method. Due to time constraints imposed by the need to keep sampling timelines on schedule, a modified equal-width-increment (EWI) sampling method was employed. The modified EWI method involved ferrying the jet boat back and forth across a channel transect at low speed, while a sampler sat on the bow and carried out a series of continuous dips using a DH48. The technique did a good job of width integration, but only sampled depth to the full length of the DH48 (about 5 ft). In the few cases, a simple grab sample was collected on the river. In these cases, the boat was brought to the midchannel in fast flow and the carboy was filled at the bow from the surface. All site visit forms indicate whether a grab, modified EWI or EWI method was used.

Additional Water Quality Samples. The following additional water quality samples were collected at various Yellowstone River sites, tributaries & canals, or WWTPs: fixed and volatile solids; common ions including alkalinity; and carbonaceous BOD. Exact records for when and where these data were collected are found in the project site visit forms.

Additional Sampling at Reach Headwaters. For both the calibration (August) and validation (September) datasets, an extra water quality sampling event was undertaken at the study-reach headwater site (Rosebud West FAS @ Forsyth). This was done on the return trip to Helena, after the completion of the main sampling run. It typically took about 10 days to complete a sampling run from Rosebud West FAS to the Bell St. Bridge in Glendive (beginning to end of study reach), and in order to determine if water quality conditions had changed at the reach headwaters during this time a second sampling event was undertaken there.

Section 3.7. Hydrologic Measurements

Flow was only measured in tributaries, canals and WWTPs. No flow was measured by DEQ in the Yellowstone River itself. It was concluded that an accurate measure of flow could not be determined using our jet boat. The river was too wide (usually 300 ft or more) to secure a tag line. The boat could be anchored at intervals across the channel, which worked well for collecting water and benthic samples. However, while at anchor, the boat usually had too much port to starboard swing to allow for accurately flow measurement, so river-flow measurements were abandoned. Flow measured in the tributaries, canals and WWTPS was carried out using the 0.6-depth measurement technique. One exception was the Terry WWTP discharge, where flow out the end of the pipe was very small and a timed bucket fill was employed instead.

Section 8.0 Schedule for Completion

Five field trips were originally planned for this project. However, the length of time required to complete each field trip was longer than anticipated. Also, the cleaning &

maintenance of the YSI 6600 sondes, which was originally planned to occur as a stand-alone event, was incorporated into the calibration and validation data-collection field trips. The modified schedule (excluding travel-out and travel-back days) was as follows:

- 1) Deployment of YSI sondes: July 31-August 8, 2007
- 2) Sampling Trip No. 1 (calibration dataset): August 17-28, 2007
- 3) Sampling Trip No. 2 (validation dataset): September 11-September 23, 2007. In addition to collecting samples for the validation dataset, the YSI 6600 sondes were retrieved throughout this time period.